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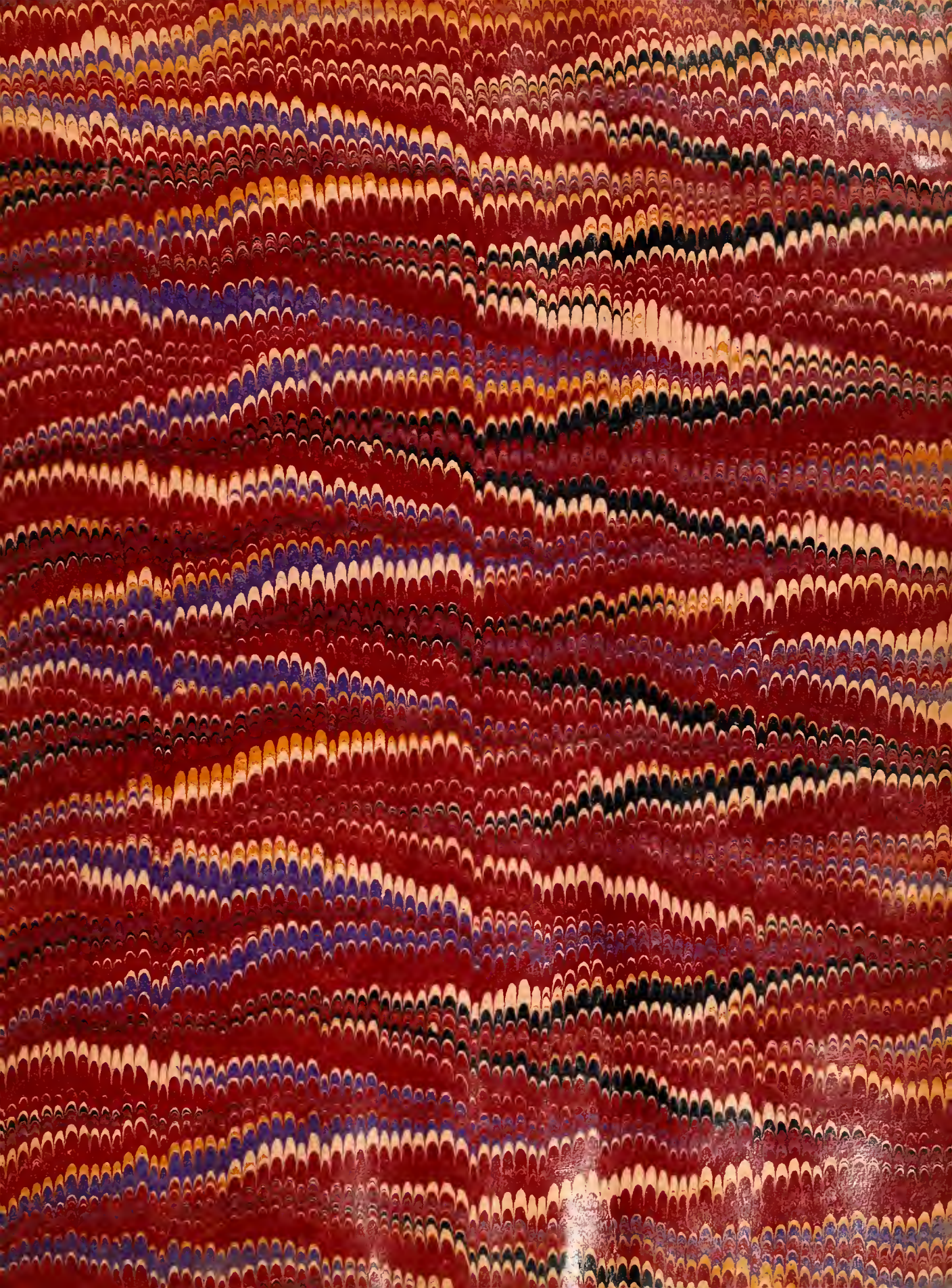

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A STUDY OF THE MOLECULAR-LOWERING of the FREEZING-POINTS of CONCENTRATED SOLUTIONS OF CERTAIN ELECTROLYTES.

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DISSERTATION

SUBMITTED to the BOARD OF UNIVERSITY STUDIES

of the

JOHNS HOPKINS UNIVERSITY

for the

DEGREE OF DOCTOR OF PHILOSOPHY

By

Frederick Hutton Getman

-: 1903 :-

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A c k n o w l e d g m e n t.

To PRESIDENT REMSEN, PROF. MORSE and to PROF. JONES the author would express his deepest gratitude for the valuable instruction received in both lecture room and laboratory. Special thanks are due Prof. Jones for suggesting and guiding this investigation.

The author would also record his appreciation of the mathematical instruction received from Prof. Hulburt.

H I S T O R I C A L R E V I E W.

In applying the freezing-point method to the then newly discovered theory of electrolytic dissociation (1 Arrhenius noted that the molecular depressions for solutions of calcium, strontium and magnesium chlorides and cadmium iodide decrease with increasing concentration to a certain minimum value and then increase again. (2 Arrhenius found that solutions of cane-sugar, dextrose, mannite and glycerine also exhibit this same phenomenon. (3 Raoult observed this abnormality in his studies on the freezing-point depressions of calcium nitrate, magnesium, sulphate and copper sulphate.

Other workers in this field have made the same observation. (4 (5 (6 Among these may be mentioned Loomis, Barnes, Jones, (7 (8 (9 Jones and Ota, Jones and Knight and Ponsot.

The first systematic study of this phenomenon however (10 was made by Jones and Chambers in 1900.

They determined the molecular depressions for solutions

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1. Ztschr. phys. Chem. 2. 496.
2. Ibid. 2. 495.
3. Ibid. 2, 488.
4. Wied. Ann. 57, 503.
5. Trans. Roy. Soc. of Canada, Vol. VI. Sec. III. 37.
6. Ztschr. phys. Chem. 12. 642.
7. Am. Chem. Jour. 22. 5 (1899)
8. Ibid. 22. 110 (1899)
9. Recherches sur les congelations. Paris (1896)
10. Am. Chem. Jour. 23-89-(1900)

of calcium, barium, strontium, magnesium and cadmium chlorides and bromides, the concentrations ranging from 1/500 normal to normal. With all the salts except cadmium chloride and bromide minima were found.

In addition to determining the molecular depressions for these solutions the authors also measured the conductivities in order to see whether there existed any irregularities in the conductivity curves in the same region where the abnormal depressions became manifest. To quote their own words "An examination of the conductivity curves shows no irregularity in the region where the molecular lowering of the freezing-point becomes a minimum. The conductivity curves are just such as would be expected for any strongly dissociated elecrolyte in water. The conductivity increases regularly from the most concentrated to the most dilute solution investigated, and shows a continually increasing dissociation with increase in dilution."

The work of Jones & Chambers was extended by Chambers and Frazer[1] who studied hydrochloric and phosphoric acids, sodium acetate, copper sulphate, zinc chloride, strontium and cadmium iodides. In each one of these cases a more or less well defined minimum was observed. In 1902 Wilhelm

1. Am. Chem. Jour. 23, 512 (1900)

Biltz[1] published the results of his further extension of the work inaugurated by Jones and Chambers. He together with Julius Meyer studied the following substances:- caesium chloride, rubidium chloride, potassium chloride, ammonium chloride, sodium chloride, lithium chloride, mercuric chloride, cupric chloride; zinc chloride, manganous chloride, nickel chloride, cobalt chloride, ferrous chloride, aluminium bromide, cupric bromide, potassium sulphocyanate, potassium cyanide, potassium bromide, potassium iodide, potassium fluoride, lithium nitrate, lithium bromide and lithium iodide.

The concentrations varied from 5/100 normal to 3/2 normal.

In almost every case well marked minima in the molecular lowerings were observed, the following salts being the exceptions:- rubidium chloride, potassium chloride, lithium chloride, aluminium bromide, potassium sulphocyanate, potassium cyanide, potassium bromide and lithium iodide.

In all of these investigations the observations have been confined to comparatively dilute solutions; in no case did the concentrations have a wider range than from extreme dilution to 3/2 normal. It seemed very desirable

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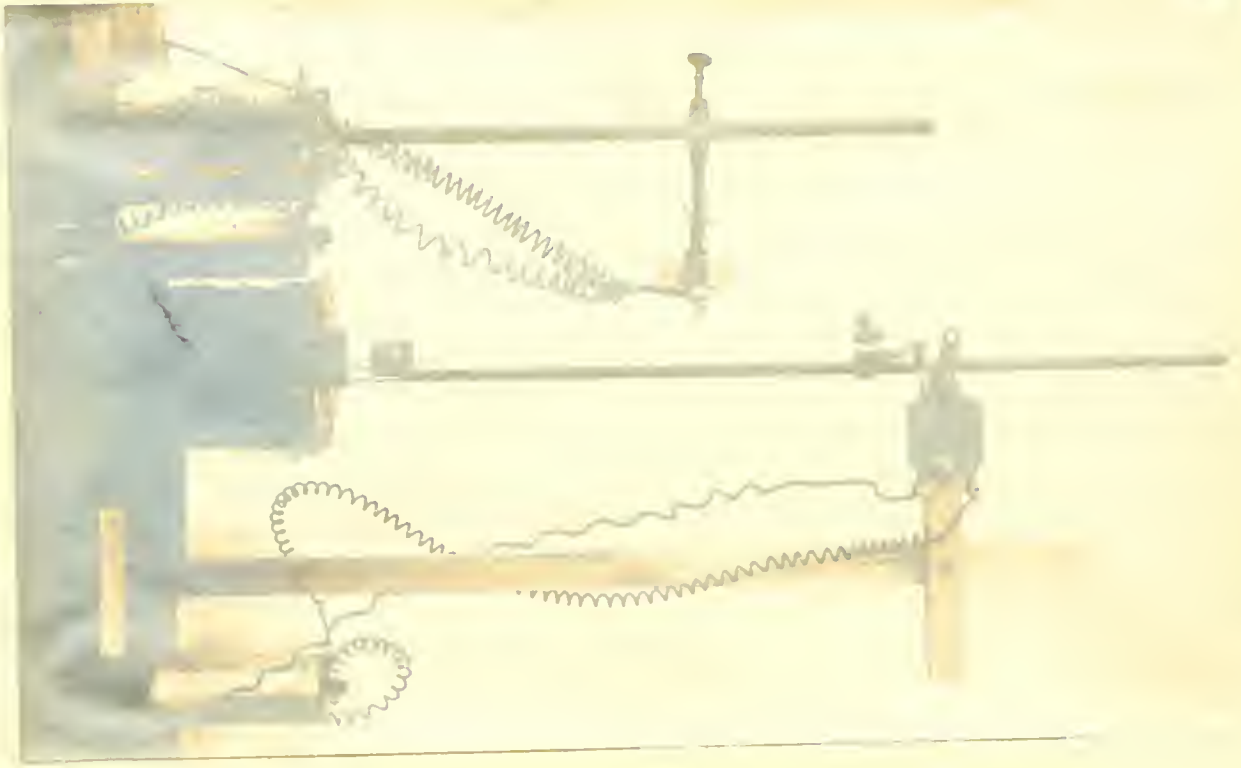
(1. Ztschr. phys. Chem. 40, 185.



to extend this work to solutions of greater concentration and to study in this way a large number of different solvents.

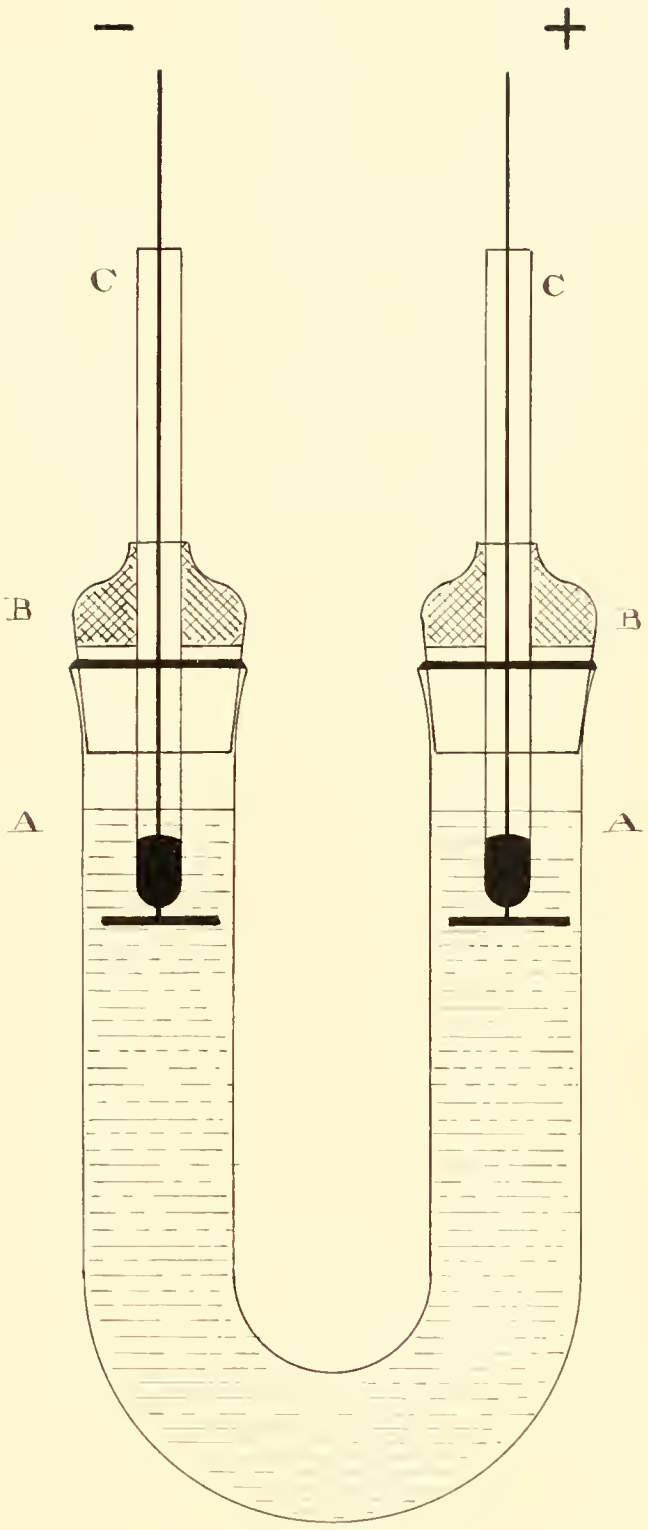
OBJECT OF INVESTIGATION.

The object of this investigation has been to extend the work of previous observers in this field by studying solutions of greater concentration by means of the freezing-point and conductivity mthods. By applying these methods to a large number of substances differing widely in chemical and physical properties it seems probable that some light may be shed upon the problems presented by concentrated solutions and that through such studies we may come to understand why the laws which obtain for dilute solutions fail completely when applied to solutions of greater concentration.

APPARATUS.

FREEZING-POINT APPARATUS:-

The accompanying figure shows the apparatus used in determining the freezing-point of the solutions. It will be seen to be essentially that devised by Beckmann. The


−
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C
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A
A

thermometers used were made expressly for this work. They were of the Beckmann type, one having a range of twelve degrees, each degree being divided into fiftieths, the other having a range of twenty-five degrees, each degree being divided into twentieths. The thermometer with the greater range was employed when working with concentrated solutions which gave a large depression while the more finely divided instrument was used with the more dilute solutions.

The stirrer in the freezing tube consisted of a ring of stout platinum wire around which was wrapped a spiral of fine platinum wire. The size of the ring was such that when wrapped with the smaller wire it would just touch the walls of the freezing-tube and thus hinder the formation of an ice sheath. This device was found to give perfect satisfaction and to be in every sense superior to the ordinary glass stirrer. The platinum stirrer was attached to a glass rod which passed closely through a glass tube in the cork of the freezing tube. In this way the movement of the stirrer was guided and cramping prevented. The freezing-tube consisted of a large test tube of 80 cc. capacity. The freezing tube was surrounded by a second glass tube giving an air space between the two of about a centimetre.

This outer tube was surrounded by the freezing mixture which was contained in a large battery jar wrapped in felt

to prevent radiation.

The freezing mixture was varied to suit the conditions, the solutions of lower concentrations freezing with a mixture of salt and ice while those of great concentrations often required the use of crystallized calcium chloride and ice.

By means of a small electric hammer uniform and gentle blows were delivered on the top of the thermometer during the time of an observation thus overcoming the friction of the mercury in the capillary.

To facilitate the reading of the thermometer a small lens magnifying several diameters was employed and more intense illumination of the thermometer scale was obtained by means of a small incandescent lamp. A thermometer graduated to tenths served to indicate the temperature of the freezing-mixture, the effort being made to keep this only a few degrees lower than the freezing temperature of the solution under observation.

CONDUCTIVITY APPARATUS:

The conductivity measurements were made by the well known Kohlrausch method using the Wheatstone bridge,

inductorium and telephone. Two types of cells were used. For the more dilute solutions the ordinary Arrhenius cell was employed but for the very concentrated solutions a specially designed cell was used. The accompanying sketch shows this cell in section.

The U-tube AA is 8 cm in length and 2.8 cm in diameter. The ground stoppers BB are filled with paraffine which serves to hold the tubes CC rigidly in place, thus insuring a constant distance between the electrodes. Each stopper is numbered corresponding to a number placed on the ends of the U-tube, so that the electrodes may not be interchanged. Furthermore by means of fine vertical lines cut on each stopper and the necks of the U-tube, the electrodes can be returned to exactly the same positions each time. That there is no alteration in the distance between the electrodes was carefully established by a series of determinations of the cell constant on successive days with the result that the differences were well within the limit of experimental error. The electrodes are of thick sheet platinum and are 2.5 cm in diameter.

All of the conductivity measurements were made at 0° C. The bath by which the solutions were maintained at this temperature was prepared in the following manner:-

A glass battery-jar was filled with finely crushed ice to which was added a small volume of water. This jar was placed in a large water-bath and the space between was packed with well crushed ice. By this means it was found easy to maintain the solution in the conductivity cell within 1/10 of a degree of the true zero. The ice in the battery jar was stirred occasionally and the temperature of the bath was noted frequently to insure the measurements being taken at 0°.

At a later stage of the work it seemed very desirable to supplement the freezing-point and conductivity measurements with determinations of the boiling-point elevations and the refractive indices of some of the solutions. For the former determinations the boiling-point apparatus devised by Jones[1] was employed while for the refraction measurements use was made of the well known Pulfrich refractometer.

With the exception of the pipettes the volumetric apparatus used was specially made and carefully calibrated for this investigation.

The volumetric apparatus employed consisted of a series of measuring flasks and a burette and a series of pipettes. The pipettes were never used in making the dilutions.

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1) Am. Chem. Jour. 19. 581. (1897)

S O L U T I O N S.

The method of preparing the solutions varied somewhat according to the solute employed but in general it may be said that a solution of two or three gram molecular weights to the liter was first made and from this by successive dilutions the less concentrated solutions were obtained. Wherever possible the mother solution was made up by direct weighing. When this was not the case the solution was standardized either by gravimetric or volumetric methods.

Great care was taken to insure the accurate standardization of the mother solution and the dilutions were made with large enough volumes to minimize errors in burette readings and flask adjustments.

The water which was used as a solvent was of a high degree of purity. The ordinary tap water was first distilled in the laboratory still and then redistilled from a dilute solution of chromic acid. This second distillate was then distilled a third time according to the method of Jones and Mackay. The water thus obtained was preserved in a large bottle which previously had been subjected to most careful cleaning. The water showed an average conductivity of 2 x 10-6.

METHODS.

FREEZING-POINT METHOD.

The practical details of the freezing-point method may be set forth most clearly by a description of the determination of the freezing-point of water by which the zero-point of the thermometer is established prior to making any measurements upon solutions.

The freezing-tube is filled to a depth of 5 cm with pure distilled water and the thermometer and stirrer inserted. The tube is then placed in a vessel containing ice and salt and the stirrer agitated frequently until ice separates. The tube is then removed and warmed until the ice just melts. It is then placed in the freezing-jacket which is surrounded with finely crushed dry ice to which has been added just enough salt to bring the temperature of the mixture to a few degrees below the freezing-point of the solvent, in this case zero.

The stirrer is agitated from time to time until freezing begins when the strring is continued vigorously and at the same time the electrical hammer is set in action. The thermometer scale is illumined by the incandescent lamp and the reading is taken after the mercury column has

remained stationary for about thirty seconds. It was almost always noticed that the solvent undercooled several degrees and it frequently was necessary to add a small fragment of ice to induce freezing.

In the case of solutions the tendency to undercool was not so marked. Owing to the change in concentration due to the separation of ice a correction was introduced. The determination of the freezing-point of the solvent as well as of any solution was repeated several times and the mean of these results taken as the true freezing-point.

CONDUCTIVITY METHOD:

The solution was introduced into the conductivity cell, care being taken to avoid the collection of air bubbles on the electrodes, and the cell was then placed in the zero bath where it was allowed to remain for half an hour, this having been found to be sufficient time for the solution to acquire the uniform temperature of zero degrees. The conductivity was then determined by the well known Kohlrausch method.

In the more concentrated solutions it was not found necessary to introduce a correction for the slight conductivity of the water.

BOILING-POINT METHOD:

Care was taken to use this method only on days when the height of the barometer remained quite constant. The general method of [1] carrying out a boiling-point measurement was employed, care being taken that the solutions boiled evenly and that the thermometer was gently tapped before reading.

The boiling-point as recorded is the mean of a series of readings taken at intervals of thirty seconds and with each determination is recorded the corresponding barometric height.

REFRACTIVITY METHOD:

The determination of refractive indices was made with the refractometer of Pulfrich. Sodium light was employed and care was taken to have the solutions at uniform temperature. The readings were made to minutes of arc and by means of the well known formula $n = \sqrt{N - \sin^2 i}$ The indices of refraction were calculated.

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1) Am. Chem. Jour. 19. 581.

ERRORS.

In order to freeze solutions of relatively great concentrations it was found necessary to do away with the extra jackets used in working with dilute solutions. This source of error became manifest when the attempt was made to determine the freezing-points of solutions having concentrations less than semi-normal. This error diminishes as the concentration increases.

It was further found to be quite impossible to use more than 30 ccm. of solution, this limitation introducing another source of error. The difficulty experienced in keeping at a minimum the difference between the temperature of the freezing-mixture and the freezing temperature of the solution was at times very great. This was particularly noticeable when calcium chloride was used in the place of salt. This source of error frequently was so large as to render it extremely difficult to obtain concordant readings in two successive determinations.

The correction introduced for the increase in concentration due to the separation of ice was the cause of some error. The amount of ice formed being a function of the degree of undercooling, it has been found practicable in working with dilute solutions to apply the correction formula $f = \frac{su}{l}$ to the observed depression.

In this formula s is the specific heat of the liquid, u the undercooling observed and l the latent heat of fusion of the solvent. The amount by which the solution will be concentrated is f from which is calculated the correction k. In more concentrated solutions, however, it is an open question whether this correction should be applied. The solution continues to lose heat even after freezing commences and the heat lost is therefore greater than that measured by the undercooling and the latent heat of fusion is less for a concentrated solution than for the pure solvent, so that for a given degree of undercooling there results a greater formation of ice than would result with the pure solvent.

This point has been tested experimentally by Loomis (1 while working with 2/10 normal sodium chloride solution. Applying the correction-formula his solution appeared concentrated about 0.2 per cent, whereas by actual determination of the change in concentration he found it to be concentrated 0.3 per cent. Such an error would be greatly magnified when the formula is applied to slutions varying from normal to threefold normal. Furthermore the amount of undercooling is found to vary greatly with the same solution upon successive freezings. It has been observed

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1) Loomis. Phys. Rev. 1. 283

upon almost every solution that the degree of undercooling is governed by the amount of over-warming. This same point has been observed by Loomis.[1] This observer says: "Thus, one may effect almost any desired amount of over-cooling by properly varying the degree of overwarming." There does not seem to be any reason for this. Furthermore as is well known freezing can be induced by the introduction of a minute fragment of ice. Thus it is evident that through this two-fold means of control of the degree of undercooling marked bias can be given to the results. The effort has been made conscientiously to avoid giving this direction to the results. It must be stated, however that this correction term is by no means satisfactory and that through its use some error has been introduced.

Two thermometers were employed in this investigation, one of which was graduated to fiftieths while the other was divided into twentieths of a degree.

Estimation to hundredths was thus the closest approximation that could be obtained.

The zero of the thermometer was determined each day before making any measurements on the solutions. The errors in the conductivity measurements were so slight that

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1) Loomis. Phys. Rev. 1.283.

no record of them need be made. The refractivity measurements are affected by an error due to inequality of temperature throughout a series of determinations. This while small manifests itself in one or two of the curves to quite a marked degree.

The boiling-point method contains several sources of error. The platinum cylinder surrounding the thermometer bulb was found to cause considerable irregularity in the boiling-point of a solution. This had been observed before by Kahlenberg[1] who ascribed this variation to difference in concentration between the solution within the cylinder and that without. This is undoubtedly true but to remove the cylinder introduces a two-fold error due to radiation and the condensed solvent.

Furthermore the extremely low boiling-point constant for water renders the accuracy of the method in the more dilute solutions extremeley doubtful. Of course the changes in barometric pressure also increase the difficulties in making an accurate boiling-point determination. This latter difficulty it may be remarked is greater in this locality than in the northwestern states or on the continent of Europe, where the barometric pressure remains practically

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1) Jour. Phys. Chem. 5. 346.

constant for hours. The method gave so much trouble that it was eventually discarded as incapable of throwing much light o n the problem in hand.

One other source of error remains to be mentioned. In making up solutions of great concentrations where the dissolved substances cannot be weighed directly the strengths of the solutions were determined by either gravimetric or volumetric methods--

In either case it was necessary to dilute the mother solution at least one-hundred-fold and take from this diluted solution a sufficient volume for the determination. In this dilution and the subsequent analytical operations some error is certain to enter but it is certainly trivial in comparison with the errors previously discussed.

TABLUATION OF RESULTS.

In the tables of freezing-point measurements the symbols employed have the following significance:-

m= concentration in gram-molecular normal

s= observed freezing-point depression

k= correction for change in concentration due to separation of ice

Δ = corrected freezing-point depression

$\frac{\Delta}{m}$ = molecular freezing-point depression.

Where possible the results of other observers in the region of lesser concentrations are given, since as has been stated the method employed for concentrated solutions does not give accurate results when applied to dilute solutions.

In the tables of conductivity measurements V denotes the volume or reciprocal concentration and μ_v° the molecular conductivity at 0° C. In the tables of refractivity measurements the notation has the following meaning:

m= concentration in gram molecular normal

X= observed angle

n= index of refraction.

In the tables of boiling-point measurements the same notation is employed as in the tables for freezing-point methods.

The results are expressed by means of curves. To avoid crowding too many curves on one plate it has been thought expedient to devote one plate to each acid and its salts. By this arrangement comparison may be readily instituted between compounds of similar constitution.

HYDROCHLORIC ACID.

HCL 36.46

The hydrochloric acid used was obtained from Baker and Adamson and was found to be free from impurities. A solution of approximately 3N concentration was made up by means of the hydrometer. Its exact strength was then determined by diluting an appreciable volume one-hundred-fold and titrating successive portions by means of potassium hydroxide. The potassium hydroxide solution used had been carefully standardized against a $\frac{N}{5}$ sulphuric acid which in turn had been standardized gravimetrically by precipitation as barium sulphate. From the data thus obtained the mother solution was diluted with the proper volume of water to make it exactly 3N and this dilution was then checked by a series of titrations.

From the mother solution a series of dilutions were made thus giving the solutions required. At this point it may be well to state that these diluted solutions were preserved in hard glass bottles which had been thoroughly cleaned and steamed.

FREEZING-POINT MEASUREMENTS.

m.	1) Loomis.	2) Jones.	3) $\frac{\Delta}{m}$ Barnes.	4) Chambers & Frazer.
0.05	3.594		3.593	3.630
0.10	3.546	3.554	3.565	3.460
0.20	3.565		3.584	3.650
0.30	3.612			
0.40				3.760

m	s	k	Δ	$\frac{\Delta}{m}$
1.0	4.140	0.018	4.122	4.122
1.5	6.720	0.087	6.633	4.422
2.0	10.218	0.281	9.937	4.969
2.5	13.510	0.055	13.455	5.382
3.0	18.100	0.004	18.096	6.030

CONDUCTIVITY MEASUREMENTS.

v.	$\mu_v 0^\circ$
2.000	216.50
1.000	200.32
0.667	182.35
0.500	170.19
0.400	152.38
0.333	141.87

1) Phys. Rev. 3. 276. 2) Zeit. Phys. Chem. 12,628.
3) Trans.Roy.Soc.Can.Vol.VI.Sec.50. 4) Am.Chem.Jour.23,515.

LITHIUM CHLORIDE.

LiCl. 42.48

The lithium chloride employed was obtained from Bender and Hobein. The concentration of the mother solution was determined volumetrically by means of a standard solution of silver nitrate.

The dilutions were made in the usual manner.

Owing to the limited supply of this salt it was impossible to carry the determinations beyond normal concentration.

FREEZING POINT MEASUREMENTS.

m.	s.	k.	Δ	$\frac{\Delta}{m}$
0.06	0.250	0.010	0.240	4.067
0.12	0.450	0.010	0.440	3.667
0.24	0.865	0.003	0.862	3.592
0.59	2.245	0.003	2.242	3.800
1.18	4.800	0.001	4.799	4.066

CONDUCTIVITY MEASUREMENTS.

v.	μ
16.95	53.75
8.47	50.42
4.22	46.76
1.67	42.28
0.86	35.58

REFRACTIVITY MEASUREMENTS.

m	x	n
0.06	67° 22′	1.32438
0.12	67 16	1.32585
0.24	67 -	1.32711
0.59	66 21	1.33021
1.18	65 19	1.33526

BOILING-POINT MEASUREMENTS. [1]

m	Δ	Barom.Press.	Δ
0.0135	0.130		0.960
0.2584	0.245	constant.	0.950
0.5899	0.568		0.963
1.0500	1.063		1.010
1.6240	1.743		1.070

1) Biltz. Zeitschr. phys. Chem. 40. 208

AMMONIUM CHLORIDE.

NHCl. 53.53

The salt used was obtained from Kahlbaum and was warranted to be chemically pure.

It was dried for several days in a dessicator over phosphorus pentoxide.

The 3N, 2N and N solutions were made up by direct weighing. The less concentrated solutions were made by dilution from the normal solution. This method was followed to avoid weighing such large masses of salt.

FREEZING-POINT MEASUREMENTS.

$-\frac{\Delta}{m}$

m	Loomis [1]	Biltz. [2]
0.04	3.50	3.39
0.05	3.48	——
0.10	3.434	——
0.20	3.396	——
0.26	——	3.39
0.40	3.393	——
0.54	——	3.41

m	s	k	Δ	$\frac{\Delta}{m}$
1.0	3.75	0.020	3.730	3.730
2.0	7.55	——	7.550	3.775
3.0	11.70	——	11.700	3.900

1) Phys. Rev. 3. 276
2) Zeit. Phys. Chem. 40. 198

CONDUCTIVITY MEASUREMENTS.

v.	μ_0
5.0	68.94
2.0	66.15
1.0	64.35
0.5	59.27
0.333	58.61

REFRACTIVITY MEASUREMENTS.

m.	X.	n.
0.2	66 55	1.32750
0.5	66 18	1.33045
1.0	65 15	1.33559
2.0	63 20	1.34536
3.0	61 30	1.35508

SODIUM CHLORIDE.

Na Cl. 58.50

The sodium chloride used was prepared from ordinary salt by precipitation from concentrated solution by means of hydrochloric acid gas. The salt thus obtained was washed with a little cold water and was then dried at 120° C in an air bath.

The 3N, 2N and N solutions were made up by direct weighing, the latter serving as a mother solution for the lesser concentrations.

FREEZING-POINT MEASUREMENTS.

m	1) Loomis. $\frac{\Delta}{m}$	2) Jones. $\frac{\Delta}{m}$	3) Biltz. $\frac{\Delta}{m}$	4) Kahlenberg. $\frac{\Delta}{m}$
0.05	3.531	3.52	3.41	
0.06	3.529			
0.07	3.510			
0.08	3.501			
0.09	3.494			
0.10	3.484	3.47	3.47	3.26
0.20	3.439	3.42	3.44	
0.26				3.19
0.30				3.21
0.40			3.42	
0.50				3.24

m.	s.	k.	Δ	$\frac{\Delta}{mL}$
0.5	1.760	0.001	1.759	3.518
1.0	3.550	0.004	3.546	3.546
2.0	7.470	0.003	7.467	3.734
3.0	12.225	0.002	12.223	4.074

1) Phys. Rev. I. 279
2) Zeit. Phys. Chem.
3) Ibid. 40.199
4) Jour. Phys. Chem. 5.353.

CONDUCTIVITY MEASUREMENTS.

v.	α_{∞}
5.000	51.84
2.000	48.62
1.000	47.13
0.500	43.14
0.333	36.59

REFRACTIVITY MEASUREMENTS.

m.	x.	n.
0.2	67 1	1.32703
0.5	66 24	1.32997
1.0	65 26	1.33469
2.0	63 37	1.34389
3.0	61 59	1.35249

BOILING-POINT MEASUREMENTS. [1]

m.	Δ	Barom. Press.	$\frac{\Delta}{m}$
0.1256	0.195	754.0 min.	1.552
0.2500	0.390	"	1.160
0.3793	0.598	"	1.576
0.5046	0.820	"	1.625
0.6299	1.031	"	1.637
0.8792	1.474	"	1.677
1.1409	1.970	"	1.726
2.0130	4.471	743.5	2.221
3.1242	6.820	743.4	2.183

1) Kahlenberg. Jour. Phys. Chem. V. 362

POTASSIUM CHLORIDE.

KCl. 74.60

The salt used was prepared by repeated crystallization from a fairly pure specimen obtained from Baker and Adamson. It was then dried for several days at 110° C in an air bath, after which it was preserved in a desicatorover calcium chloride until it was required.

From the mother solution prepared by direct weighing the lesser concentrations were obtained by dilution.

FREEZING-POINT MEASUREMENTS.

m.	1) Loomis.	$\frac{\Delta}{m}$ 2) Jones.	3) Biltz.
0.05	3.50	3.50	———
0.10	3.445	3.47	3.47
0.20	3.404	—	—
0.30	—	—	3.41
0.40	3.353	—	—
0.50	—	—	3.34
0.80	—	—	3.27

m.	s.	k.	Δ	$\frac{\Delta}{m}$
0.2	0.688	0.003	0.685	3.425
0.5	1.695	0.003	0.692	3.384
1.0	3.400	———	3.400	3.400
2.0	6.950	0.006	6.944	3.472
3.0	11.065	0.003	11.062	3.687

1) Phys. Rev . 3. 276
2) Zeit. Phys. Chem.
3) Ibid. 40, 198

CONDUCTIVITY MEASUREMENTS.

v.	μ_∞
20.0	72.37
10.0	69.53
5.0	68.71
2.0	65.21
1.0	61.07
0.5	60.98

BOILING-POINT MEASUREMENTS. [1]

m.	Δ	Barom. press.	$\frac{\Delta}{m}$
0.2122	0.293	737.6 mm..	1.381
0.5124	0.700	"	1.366
0.9012	1.247	"	1.383
1.3990	2.004	"	1.432
2.0170	2.975	"	1.475
2.4160	3.653	"	1.512
2.7720	4.266	"	1.539
3.1840	5.009	"	1.570

CALCIUM CHLORIDE.

$CaCl_2$-- 110.8

The salt was obtained from Fimer and Amend in a well crystallized condition. It was dissolved in enough water to insure the solution having a concentration of at least 5/2N. By means of several gravimetric determinations of calcium the exact strength of the mother solution was obtained. It was then diluted to 5/2N and the calcium redetermined as a check. From this mother solution the other solutions were prepared by dilution.

It may be noted at this point that owing to the extremely large depressions produced by concentrated solutions of this substance, it was necessary to employ crystallized calcium chloride and ice as the freezing mixture and even then determinations beyond 2N were quite impossible.

FREEZING-POINT MEASUREMENTS.

m.	$\frac{\Delta}{m}$ Loomis.[1]	Jones & Chambers.[2]
0.05	4.85	———
0.10	4.80	4.98
0.20	4.84	4.96
0.30	———	5.02
0.40	———	5.16
0.50	5.19	5.26

m.	s.	k.	Δ	$\frac{\Delta}{m}$
1.0	6.350	0.005	6.345	6.345
1.5	11.300	0.004	11.296	7.531
2.0	17.875	0.008	17.867	8.934

CONDUCTIVITY MEASUREMENTS.

v.	μ_{25}°
1.000	71.13
0.667	62.14
0.500	53.98
0.400	44.79

1) Phys. Rev. 4. 298
2) Am. Chem. Jour. 23.93

STRONTIUM CHLORIDE.

$SrCl_2$. 158.5

The salt used was obtained from Baker and Adamson. It was purified by repeated crystallizations and finally dried at 110° C. It was preserved in a dessicator over calcium chloride until required.

The mother solution was made up by direct weighing and then analyzed for both strontium and chlorine as a check. The dilutions were made in the usual manner.

FREEZING-POINT MEASUREMENTS.

m.	$\frac{\Delta}{n\upsilon}$ Loomis.[1]	Jones & Chambers.[2]
0.05	4.90	5.16
0.10	4.85	4.88
0.20	4.82	4.87
0.30	———	4.90
0.40	———	4.95
0.50	5.08	5.09

m.	s	k	Δ	$\frac{\Delta}{n\upsilon}$
1.0	6.010	0.010	6.000	6.000
1.5	10.725		10.725	7.150
2.0	16.425	0.003	16.422	8.211

CONDUCTIVITY MEASUREMENTS.

v.	μ_v^{0}
2.000	84.26
1.000	74.57
0.667	63.01
0.500	55.26

1) Phys. Rev. 4.278
2) Am. Chem. Jour. 23.94

BARIUM CHLORIDE.

$BaCl_2$. 208.3.

The salt obtained from Baker and Adamson in a relatively pure condition. It was recrystallized several times and then dried for some hours at 110° C in the air bath.

The mother solution was made up by direct weighing and the lesser concentrations obtained by dilution. The slight solubility of the salt prevented the study of concentrations beyond 3/4 N.

FREEZING-POINT MEASUREMENTS.

m.	Loomis.[1] $\frac{\Delta}{mc}$	Jones & Chambers.[2]
0.05	4.770	———
0.10	4.690	4.85
0.20	4.655	4.77
0.30	———	4.82
0.50	4.830	4.95

m	s	k	Δ	$\frac{\Delta}{mc}$
0.5	2.500	0.007	2.493	4.986
0.75	3.860	0.003	3.857	5.143

CONDUCTIVITY MEASUREMENTS.

v.	μ_v^0
20.000	116.05
10.000	103.79
4.000	95.94
2.000	89.24
1.333	85.27

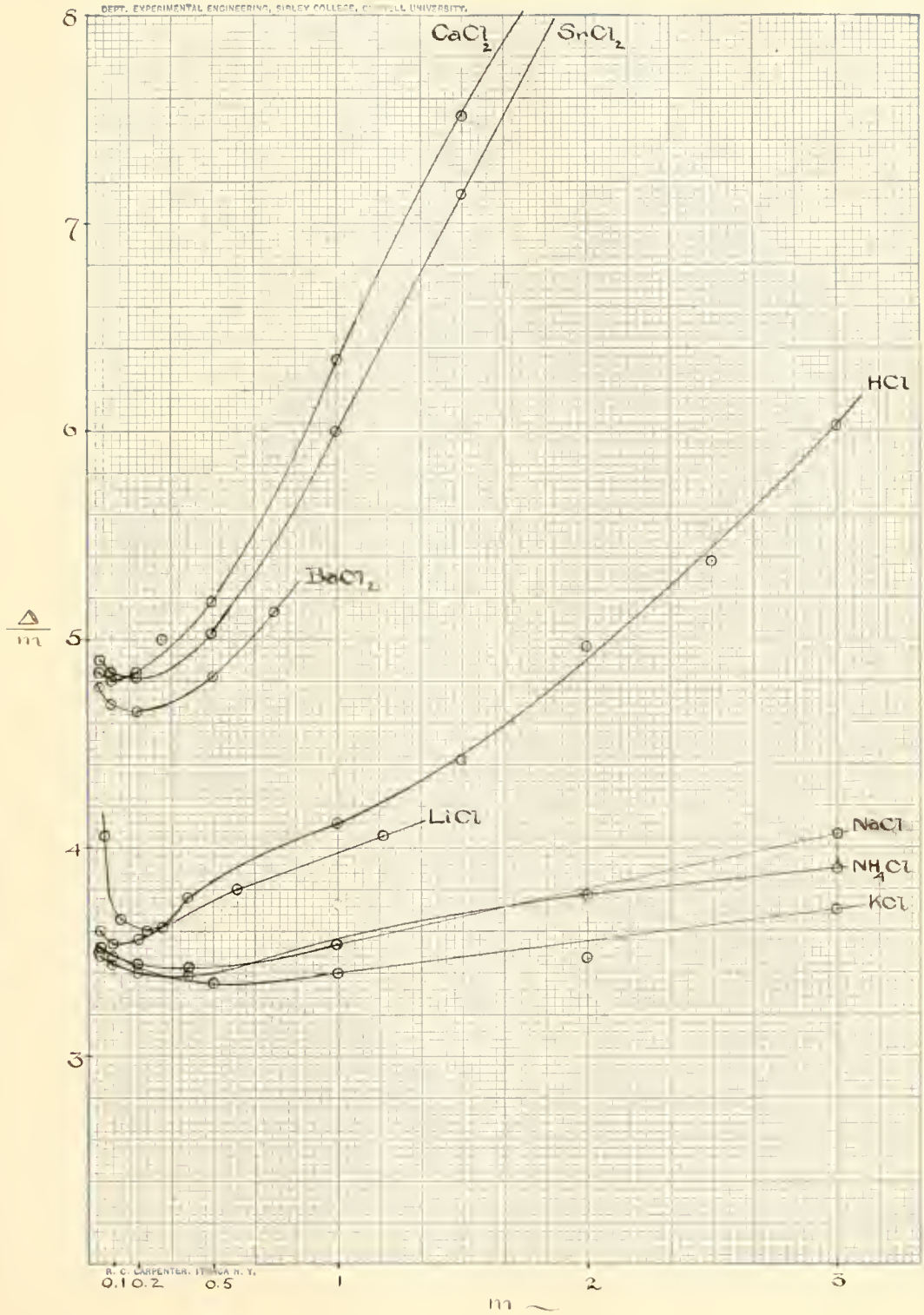
1) Phys. Rev. 3. 277--

2) Am. Chem. Jour. 23.94

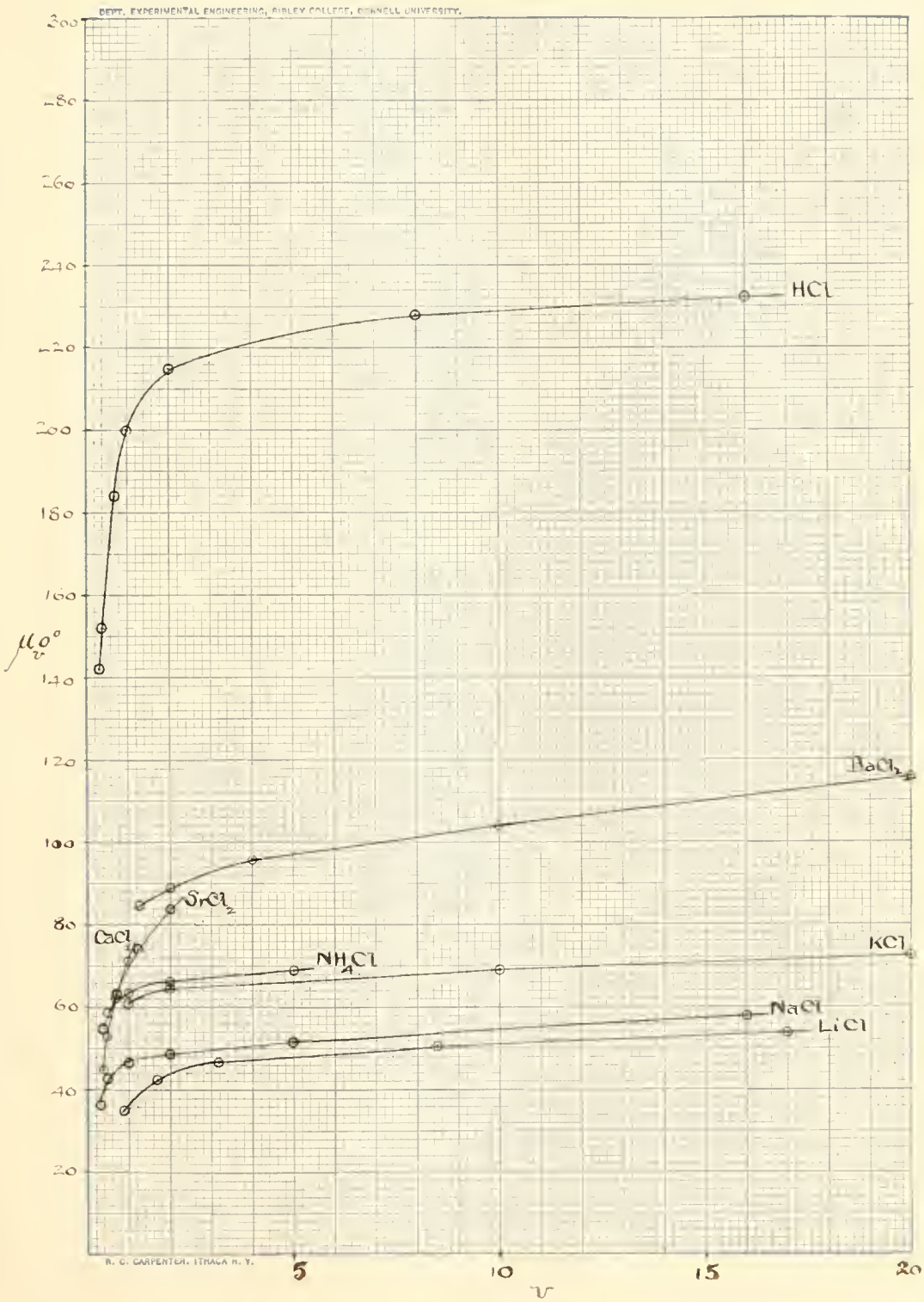
BOILING-POINT MEASUREMENTS.[1]

m	Δ	Barom. Press	$\frac{\Delta}{m}$
0.3397	0.208	752.8 m .	0.612
0.8290	0.496	"	0.598
1.3612	0.839	"	0.616
1.9868	1.293	"	0.651
2.7071	1.909	"	0.705
3.5036	2.517	"	0.718

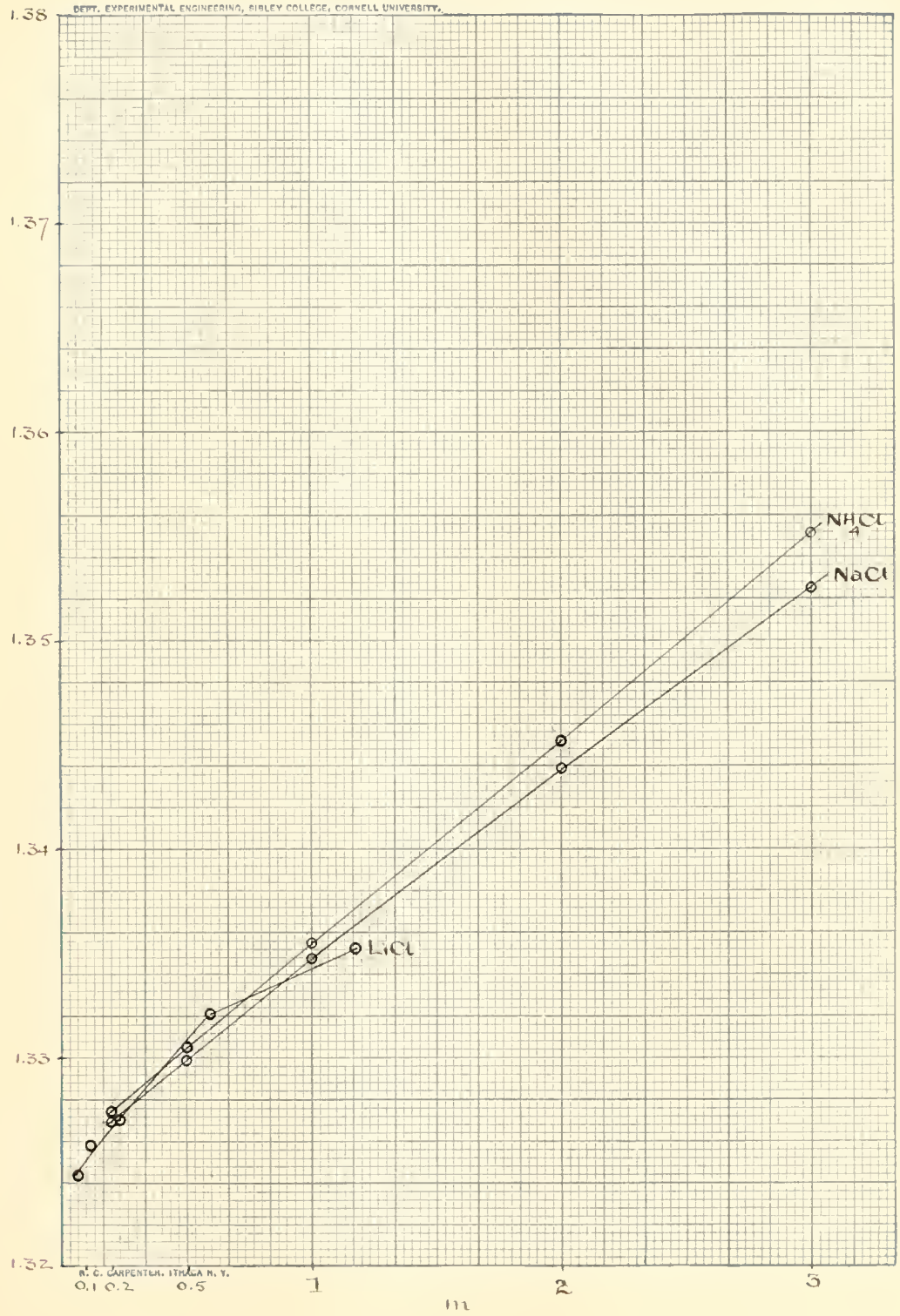
1) Kahlenberg. Jour. Phys. Chem. V. 366



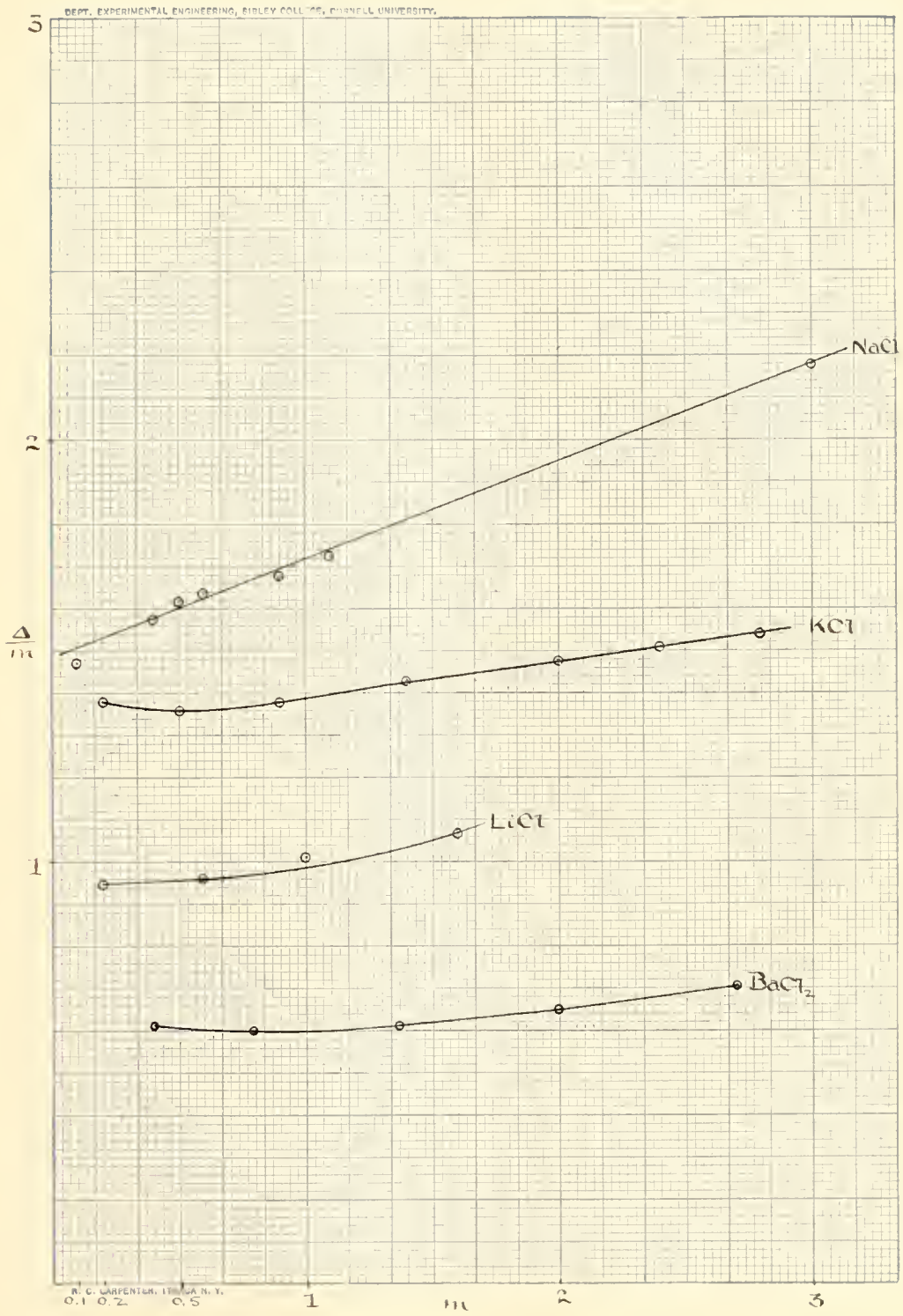
Freezing-Point Lowerings for the Chlorides



Conductivity Curves for the Chlorides



Refractivity Curves for the Chlorides—



Boiling-Point Curves for the Chlorides

NITRIC ACID.

HNO_3 63.05

The acid used was obtained from Baker and Adamson. By means of the hydrometer and Lunge's Tables a solution approximately 3N was made up. This solution was then accurately standardized by means of potassium hydroxide, the same method being used as in the case of hydrochloric acid.

From the mother solution thus prepared the more dilute solutions were obtained.

FREEZING-POINT MEASUREMENTS.

m.	$\frac{\Delta}{nc}$ 1) Jones.	2) Loomis.
0.05	3.71	3.51
0.10	3.53	3.50
0.20	—	3.48

m	s	k	Δ	$\frac{\Delta}{nc}$
0.5	1.840	0.018	1.822	3.644
1.0	3.850	0.054	3.796	3.796
1.5	5.980	0.042	5.938	3.959
2.0	8.425	0.015	8.410	4.205
2.5	11.125	0.079	11.046	4.418
3.0	14.058	0.150	13.908	4.636

CONDUCTIVITY MEASUREMENTS.

v.	$\mu_v o^\circ$
2.000	213.30
1.000	194.95
0.667	184.89
0.500	169.23
0.400	155.43
0.333	140.97

1) Zeit. Phys. Chem. 12. 23
2) Phys. Rev. 4. 282

LITHIUM NITRATE.

$LiNO_3$ 69.07

The sample of lithium nitrate used was obtained in well crystallized form from Bender and Hobein. It was heated to 120° C for several days in an air bath and was then allowed to cool in a desiccator over calcium chloride. When cool the mother solution was prepared by direct weighing of the salt, care being taken to make the weighing as expeditiously as possible after the removal of the salt from the desiccator.

Owing to the limited supply of this salt the mother solution contained only one gram molecule of dissolved substance in a liter.

FREEZING-POINT MEASUREMENTS.

m	s	k	Δ	$\frac{\Delta}{m}$
0.05	0.185	0.002	0.183	3.660
0.10	0.355	0.002	0.353	3.530
0.20	0.745	0.023	0.722	3.610
0.30	1.095	0.001	1.094	3.647
0.40	1.465	0.003	1.462	3.655
0.50	1.860	0.005	1.855	3.710
0.60	2.275	0.008	2.267	3.778
0.70	2.665	0.002	2.663	3.804
0.80	3.135		3.135	3.919
0.90	3.560	0.003	3.557	3.952

CONDUCTIVITY MEASUREMENTS.

v	μ_∞
20.00	50.00
10.00	47.56
5.00	45.91
3.33	44.05
2.50	43.90
2.00	42.50
1.67	40.81
1.43	39.91
1.25	39.89

AMMONIUM NITRATE.

NH_4NO_3 - 80.12

The salt was obtained from Baker and Adamson in a comparatively pure condition and was recrystallized several times. It was then dried at 100°C and preserved until needed in a desiccator over calcium chloride.

The mother solution was prepared by direct weighing and from it the successive dilutions were made.

FREEZING POINT MEASUREMENTS.

m	$\frac{\Delta}{m}$ Loomis 1)
0.025	3.49
0.050	3.47
0.100	3.424
0.200	3.321

m	s	k	Δ	$\frac{\Delta}{m}$
0.5	1.690	0.004	1.686	3.372
1.0	3.150	0.005	3.145	3.148
2.0	6.000	0.004	5.996	2.998
3.0	8.725	0.005	8.720	2.906

1) Phys. Rev. 3. 279

CONDUCTIVITY MEASUREMENTS.

v	
20.0	67.49
10.0	65.05
5.0	63.44
2.0	60.26
1.0	54.97
0.5	52.81

REFRACTIVITY MEASUREMENTS.

m	X	n
0.05	67° 22	1.32538
0.10	67 21	1.32585
0.20	67 3	1.32687
0.50	66 25	1.32989
1.00	65 24	1.33485
2.00	63 30	1.34449

SODIUM NITRATE.

$NaNO_3$ - 85.09

The sample of sodium nitrate used was obtained from Baker and Adamson and was purified by repeated crystallizations. The purified salt was dried at 110° C in an air bath and preserved until required over calcium chloride in a desiccator.

The mother solution was made up by direct weighing and the other solutions obtained from this by dilution.

FREEZING-POINT MEASUREMENTS.

m	$\frac{\Delta}{m}$ Loomis. 1)
0.05	3.44
0.10	3.428
0.20	3.345

m	s	k	Δ	$\frac{\Delta}{m}$
1.0	3.200	0.002	3.198	3.198
1.5	4.670	0.001	4.669	3.113
2.0	6.150	0.003	6.147	3.074
2.5	7.470	0.002	7.468	2.987
3.0	8.913	0.004	8.909	2.969

CONDUCTIVITY MEASUREMENTS.

v	μ_{25}°
2.000	44.90
1.000	40.41
0.667	36.90
0.500	34.16
0.400	30.96

1) Phys. Rev. 3. 279

POTASSIUM NITRATE.

KNO. 101.19--

The specimen of potassium nitrate was obtained from Baker and Adamson in a fair state of purity. This was recrystallized until it no longer gave a flame-test for sodium. It was then dried for several days at 110° C in an air-bath, after which it was preserved in a desiccator over calcium chloride until required for use.

The mother solution was made up by direct weighing and the remaining solutions made by dilution.

FREEZING-POINT MEASUREMENTS.

m	Loomis.[1]
0.05	3.41
0.10	3.314
0.20	3.194

m	s	k	Δ	$\frac{\Delta}{m}$
0.4	1.295	0.037	1.258	3.145
0.5	1.553	0.016	1.537	3.074
1.0	2.730	0.001	2.729	2.729

CONDUCTIVITY MEASUREMENTS.

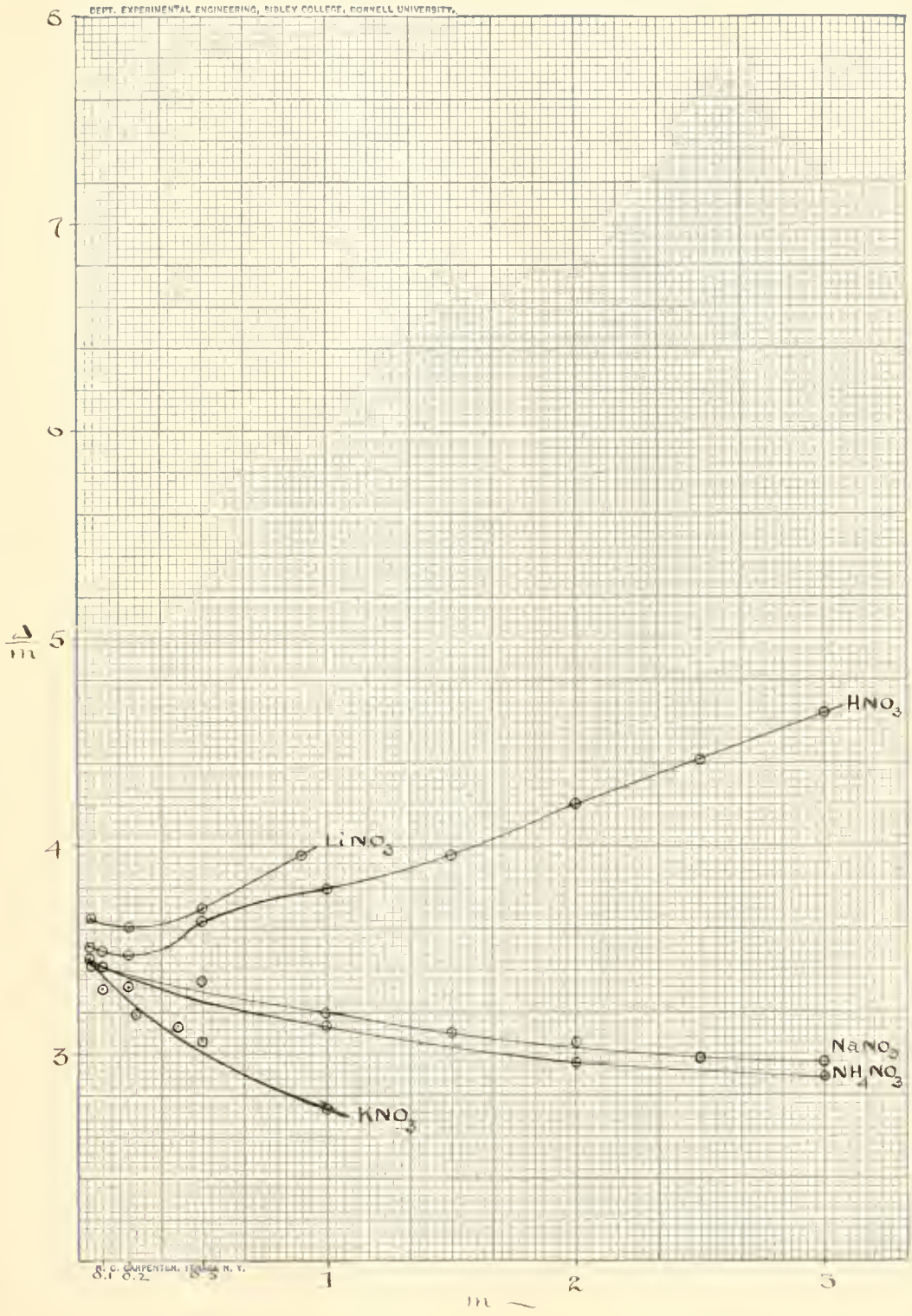
v	$\lambda_{25°}$
2.000	53.20
1.000	49.97
0.667	46.30

1) Phys. Rev. 3. 278.

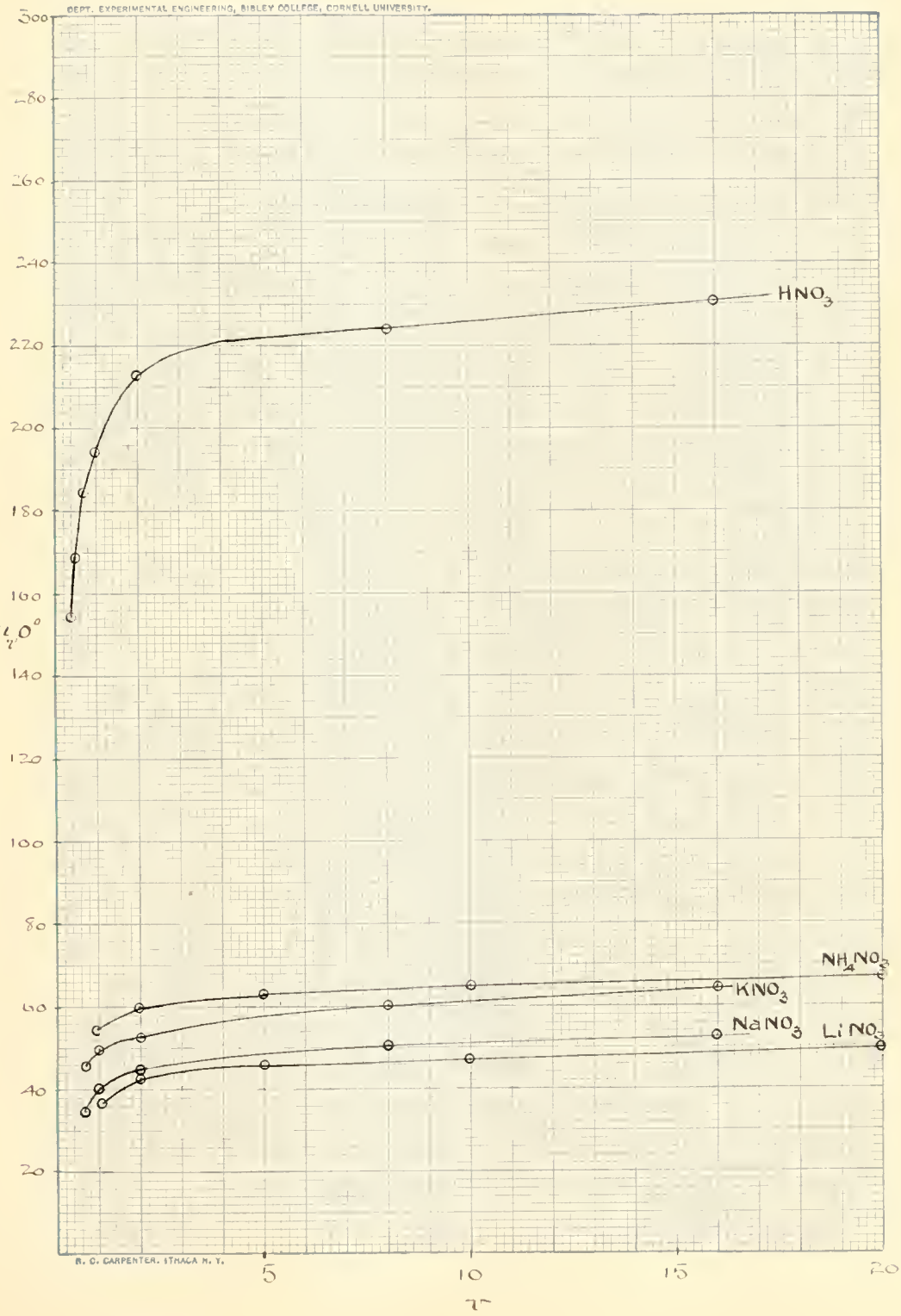
BOILING-POINT MEASUREMENTS. [1]

m	Δ	Barom. press.	$\frac{\Delta}{m}$
0.2789	0.248	741.1 mm..	0.889
0.6058	0.518	"	0.855
0.9721	0.822	"	0.845
1.4798	1.207	"	0.815
2.1333	1.706	741.2	0.795
2.7095	2.123	"	0.783

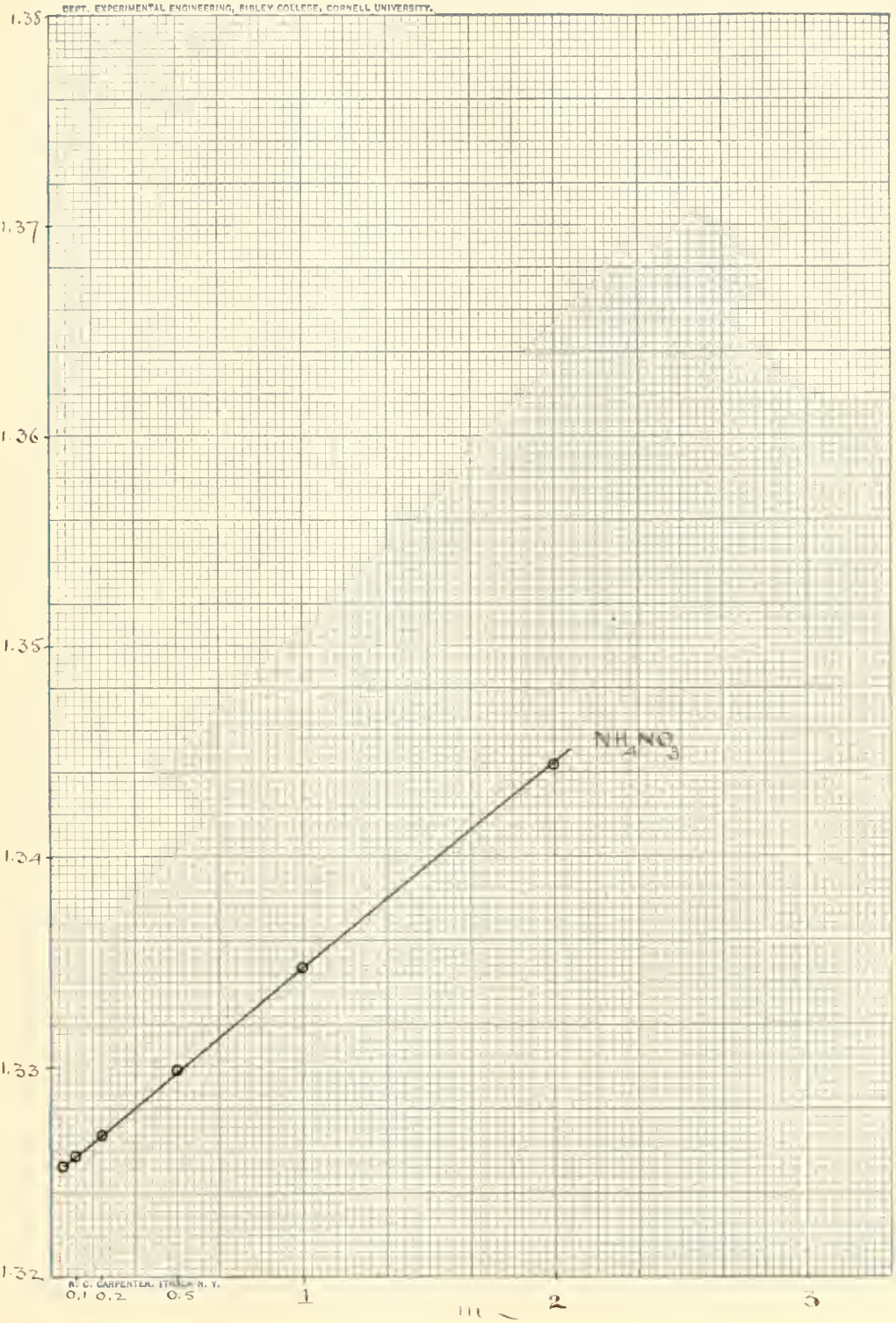
1) Kahlenberg. Jour. Phys. Chem. Y.368.



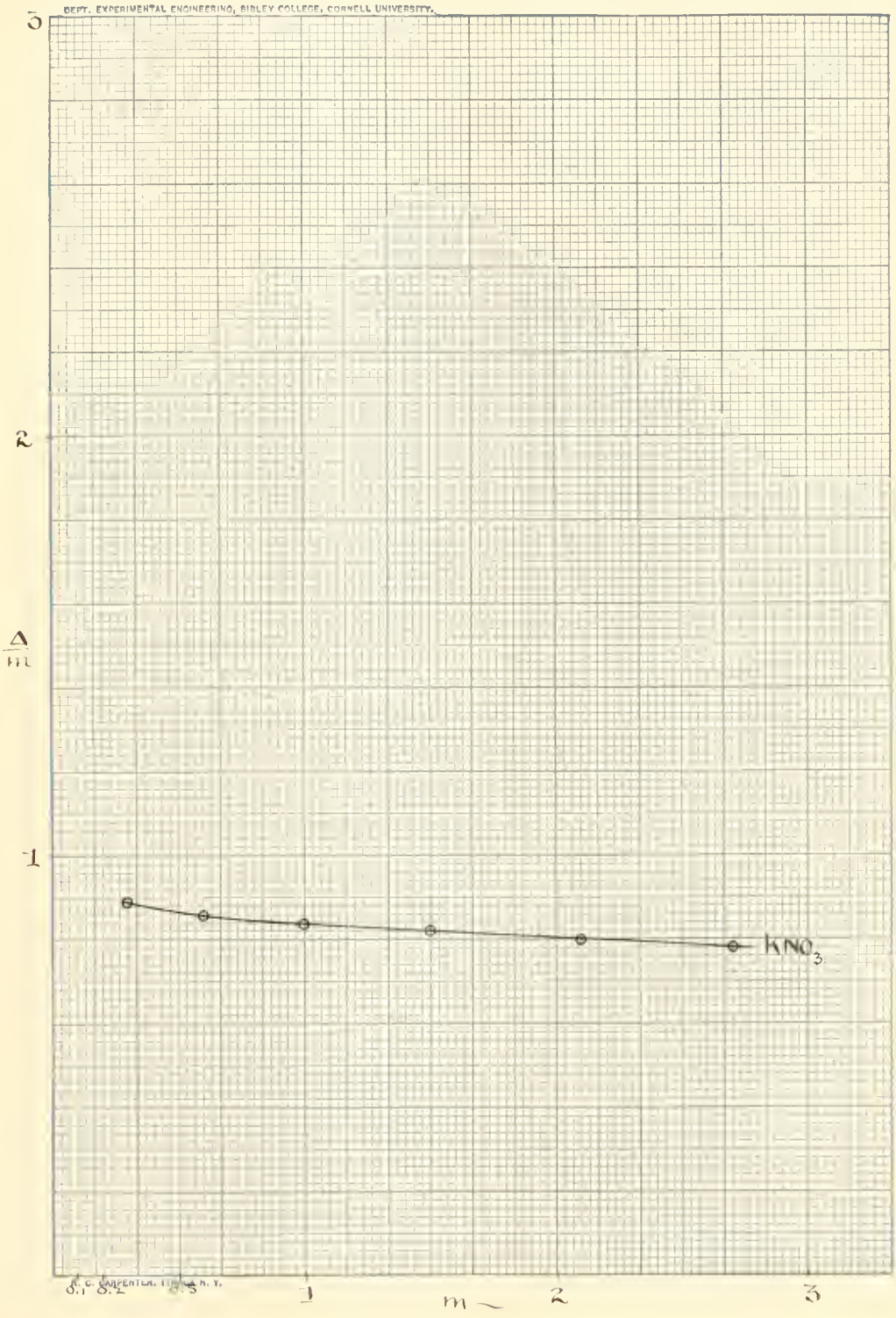
Freezing-Point Curves for the Nitrates.



Conductivity Curves for the Nitrates.



Refractivity Curves for the Nitrates



Boiling-Point Curves for the Nitrates.

SULPHURIC ACID.

H_2SO_4 98.08

The acid used was obtained from Baker and Adamson and was free from the ordinary impurities.

By means of the hydrometer and Lunge's Tables a solution approximately 3N was made up. A portion of this solution was then diluted a hundred-fold and successive portions of this diluted solution were removed for titration with N/5 potassium hydroxide. When the exact strength of the solution was obtained it was diluted sufficiently to make the solution strictly 3N--

This solution was then checked by several titrations. As has been said the potassium hydroxide solution used for the titration was standardized by means of N/5 sulphuric acid which in turn was standardized gravimetrically.

The dilutions from the mother solution were made as usual.

FREEZING-POINT MEASUREMENTS.

m	Loomis.[1]	Jones.[2] $\frac{\Delta}{m}$	Barnes.[3]
0.05	4.130	———	4.167
0.10	3.968	3.945	3.961
0.20	3.850	———	3.883

m	s	k	Δ	$\frac{\Delta}{m}$
0.10	0.413	0.016	0.397	3.970
0.30	1.180	0.024	1.156	3.853
0.50	2.040	0.023	2.017	4.034
1.00	4.203	0.014	4.189	4.189
1.50	7.450	0.007	7.443	4.962
2.00	11.300	0.004	11.296	5.648
2.50	16.275	———	16.275	6.510

1) Phys. Rev. I. 281.
2) Zeit. Phys. Chem.12.628.
3) Trans. Roy. Soc. Canada.Vol.VI. Sec.III.50.

CONDUCTIVITY MEASUREMENTS.

V	$\mu_2 c$
2.000	277.30
1.000	253.44
0.667	221.25
0.500	199.42
0.400	178.79
0.333	155.29
0.286	135.00
0.250	118.86
0.222	100.21
0.200	86.97

AMMONIUM SULPHATE.

$(NH_4)_2SO_4$ - 114.14

The salt used was obtained from Bender and Hobein and was purified by several recrystallizations. It was dried at 100° C in an air-bath and was then preserved in vacuo over sulphuric acid until required.

The mother solution was made up by direct weighing and the lesser concentrations obtained by dilution.

FREEZING-POINT MEASUREMENTS.

m	s	k	Δ	$\frac{\Delta}{m}$
0.05	0.025	0.001	0.024	4.80
0.10	0.475	0.006	0.469	4.69
0.20	0.825	0.007	0.818	4.09
0.50	1.975	0.006	1.969	3.94
1.00	3.725	0.039	3.686	3.69
1.40	5.200	0.067	5.133	3.67

CONDUCTIVITY MEASUREMENTS.

v	Λ_v
20	100.60
10	95.84
5	86.15
2	80.08
1	72.55
0.71	69.30

REFRACTIVITY MEASUREMENTS.

m	x	n
0.05	67 15'	1.32593
0.10	67	1.32711
0.20	66 45	1.32829
0.50	65 42	1.33338
1.00	64 7	1.34131
1.40	62 49	1.34807

SODIUM SULPHATE.

$Na_2 SO_4$

The salt used was obtained from Kahlbaum. It was in the form of the decahydrate and was warranted to be chemically pure--

It was heated to 120° C for several days and was then removed from the air bath and finely pulverized in a mortar, after which it was placed over sulphuric acid in a vacuum desiccator until required. The mother solution was made up by direct weighing.

Owing to the formation of the hydrate upon cooling it was found impossible to extend the observations on the freezing-point beyond N/2 concentration.

FREEZING-POINT MEASUREMENTS.

m	$\frac{\Delta}{m}$ Loomis 1)
0.05	4.590
0.10	4.340
0.20	4.071
0.30	3.875

m	s	k	Δ	$\frac{\Delta}{m}$
0.50	1.850	0.011	1.839	3.678

CONDUCTIVITY MEASUREMENTS.

v.	μ_v 0°
20.0	93.06
10.00	84.92
5.00	73.09
2.00	60.54
1.00	47.13
0.67	36.82
0.50	28.54

1) Phys. Rev. 3. 277

REFRACTIVITY MEASUREMENTS.

m	X	n
0.05	66 13	1.32609
0.10	66 58	1.32727
0.20	66 30	1.32949
0.50	65 20	1.33518
1.00	63 37	1.34389
1.50	62 05	1.35195
2.00	60 43	1.35934

BOILING-POINT MEASUREMENTS.

m	Δ	Barom. Press.	$\frac{\Delta}{m}$
0.05	0.050	763.0 mm.	1.00
0.10	0.105	763.1 "	1.05
0.20	0.235	763.3 "	1.17
0.50	0.531	763.5 "	1.06
1.00	1.064	763.5 "	1.06
1.50	1.748	765.0 "	1.07
2.00	2.085	764.8 "	1.04

POTASSIUM SULPHATE.

K_2SO_4--

The specimen of salt used was obtained from Kahlbaum and was dried for several days in the air-bath at a temperature of 120° C and was then preserved in a desiccator over sulphuric acid until required.

The mother solution was made up by direct weight.

Owing to the excessively slight sclubility of this salt it was impossible to extend the freezing-point observation beyond 3/10 N.

It is also worthy of note at this point that the refractive indices for solutions of sodium and potassium sulphates are nearly identical as may be seen from the curves.

FREEZING-POINT MEASUREMENTS.

m	Δ 1) Loomis	2) Jones
0.05	4.540	4.61
0.10	4.317	4.28
0.20	4.067	— —
0.30	3.891	——

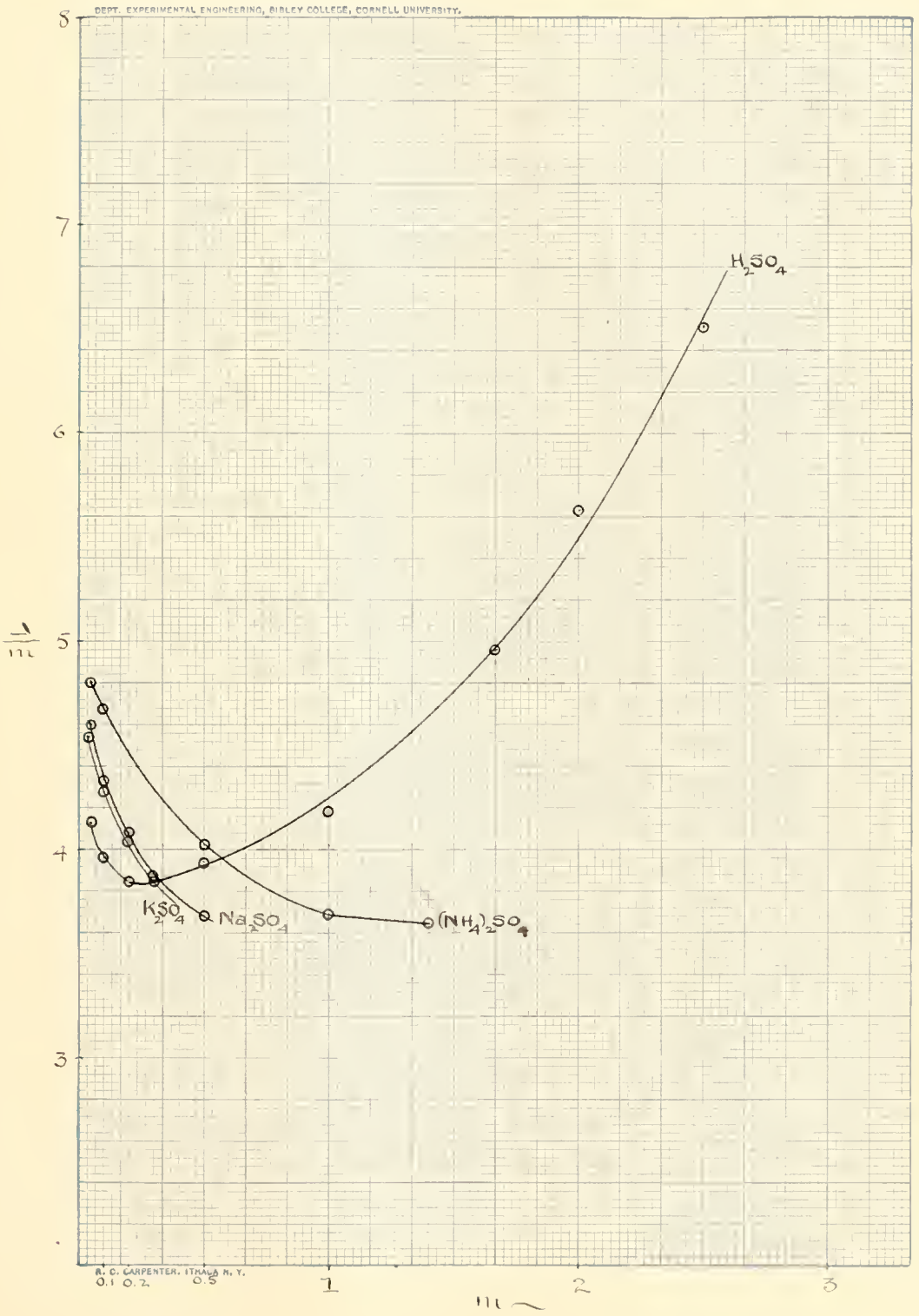
CONDUCTIVITY MEASUREMENTS.

v	μ_v
20	118.89
10	109.79
5	98.88
2	88.93

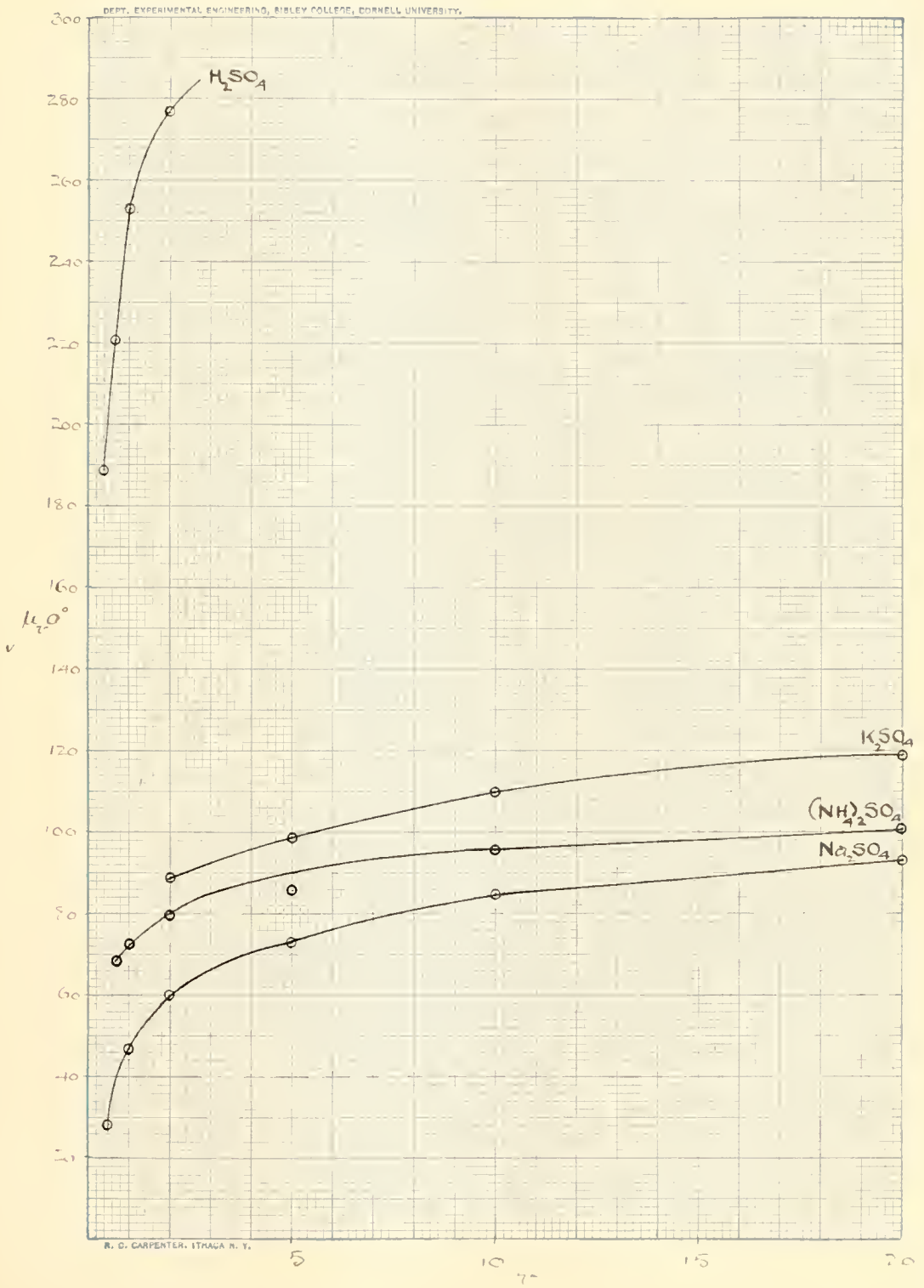
REFRACTIVITY MEASUREMENTS.

m	x	n
0.05	67° 12	1.32616
0.10	66 57	1.32735
0.20	66 30	1.32949
0.50	65 20	1.33518

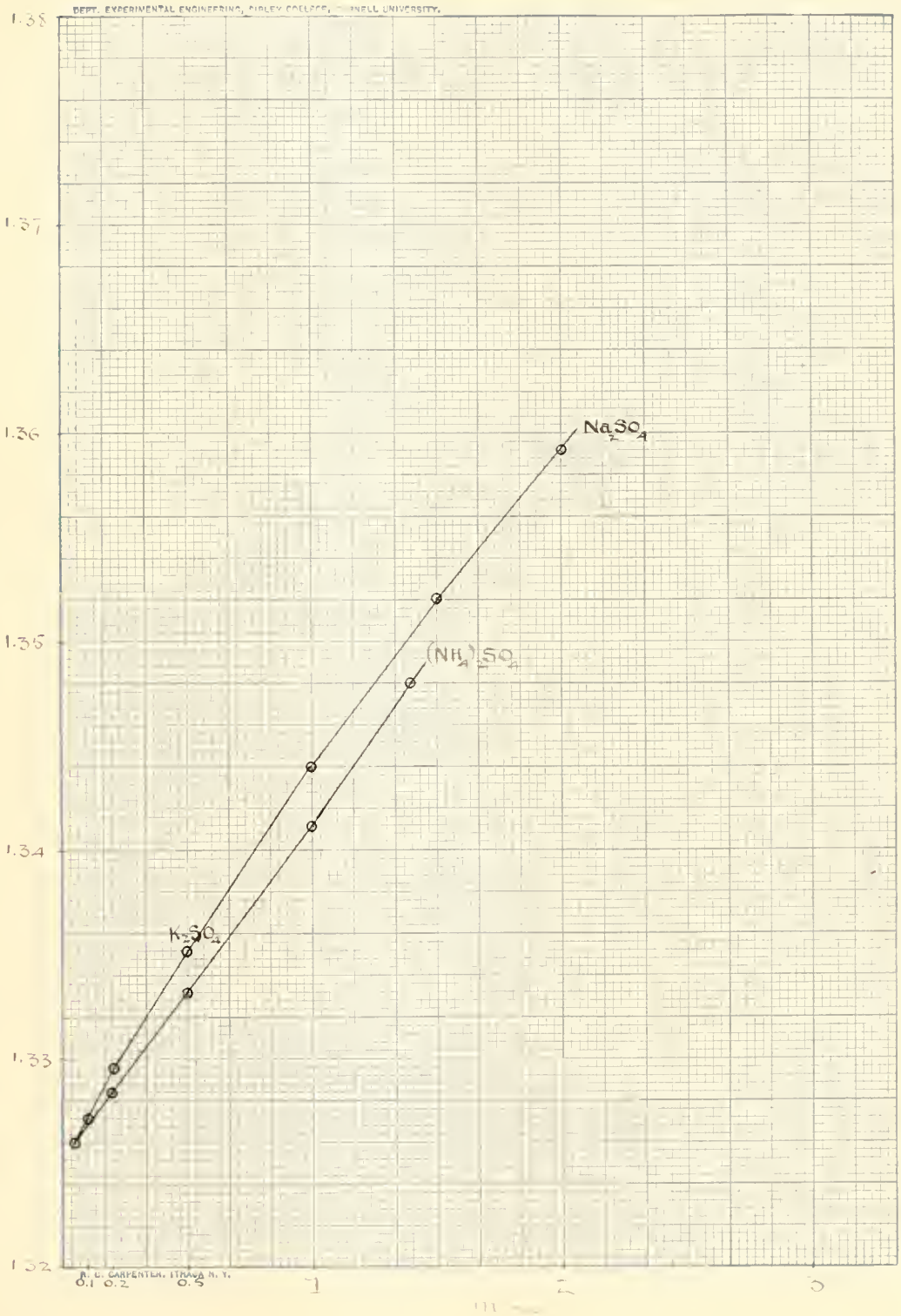
1) Phys. Rev. 3. 277.
2) Zeit. Phys. Chem. 11. 527



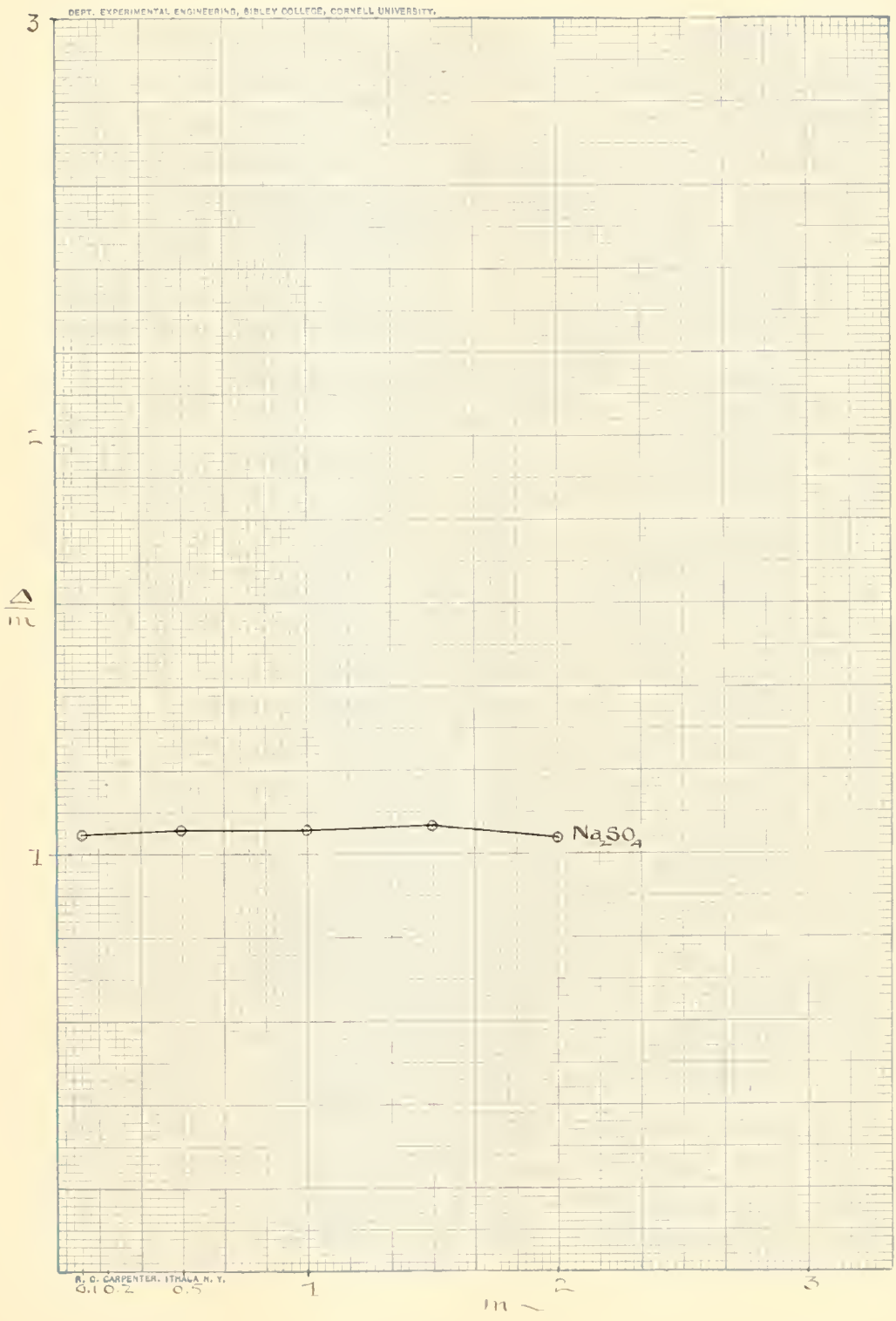
Freezing-Point Curves for the Sulphates.



Conductivity Curves for the Sulphates



Refractivity Curves for the Sulphates.



Boiling-Point Curves for the Sulphates.

SODIUM CARBONATE.

Na_2CO_3 106.1

The salt used was obtained from Kahlbaum, it being of the highest grade of chemicals. It was dried for twenty-four hours over sulphuric acid in vacuo. The solutions were made up by direct weighing and dilution. Owing to the separation of the hydrate freezing-point measurements beyond 5/10 N were impossible.

FREEZING-POINT MEASUREMENTS.

m	$\frac{\Delta}{m}$	
	1) Loomis.	2) Jones.
0.05	4.640	4.67
0.10	4.416	4.45
0.20	4.170	

m	s	k	Δ	$\frac{\Delta}{m}$
0.5	1.883	0.001	1.882	3.764

1) Phys. Rev. 3.278.
2) Zeit. Phys. Chem. 12.623.

CONDUCTIVITY MEASUREMENTS.

v	Λ_v
20	85.80
10	76.80
5	66.90
2	53.10
1	39.14
0.5	24.53

REFRACTIVITY MEASUREMENTS.

m	x	n
0.05	67° 14'	1.32601
0.10	66 57	1.32735
0.20	66 29	1.32957
0.50	65 12	1.33584
1.00	63 20	1.34536
2.00	60 13	1.36209

BOILING POINT MEASUREMENTS.

m	Δ	Barom. Press	$\frac{\Delta}{m}$
0.05	0.053	763.5 mm.	1.060
0.10	0.132	763.7	1.320
0.20	0.258	763.8	1.290
0.50	0.538	764.3	1.176
1.00	0.947	765.3	0.947
2.00	1.747	771.5	0.874

POTASSIUM CARBONATE.

K_2CO_3 138.3

The specimen used was one of Kahlbaum's chemically pure preparations. It was dried for six days in vacuo over sulphuric acid. The mother solution was made up by direct weighing and the lesser concentrations were obtained by dilution.

FREEZING-POINT MEASUREMENTS.

m	$\frac{\Delta}{m}$ 1) Loomis	$\frac{\Delta}{m}$ 2) Jones
0.05	4.710	4.75
0.06	——	4.75
0.10	4.540	4.62
0.20	4.385	——

m	s	k	Δ	$\frac{\Delta}{m}$
0.4	1.728	0.045	1.683	4.208
1.0	4.383	0.008	4.375	4.375
2.0	9.725	0.015	9.710	4.855

1) Phys. Rev. 3. 278.
2) Zeit. Phys. Chem. 12. 623.

CONDUCTIVITY MEASUREMENTS.

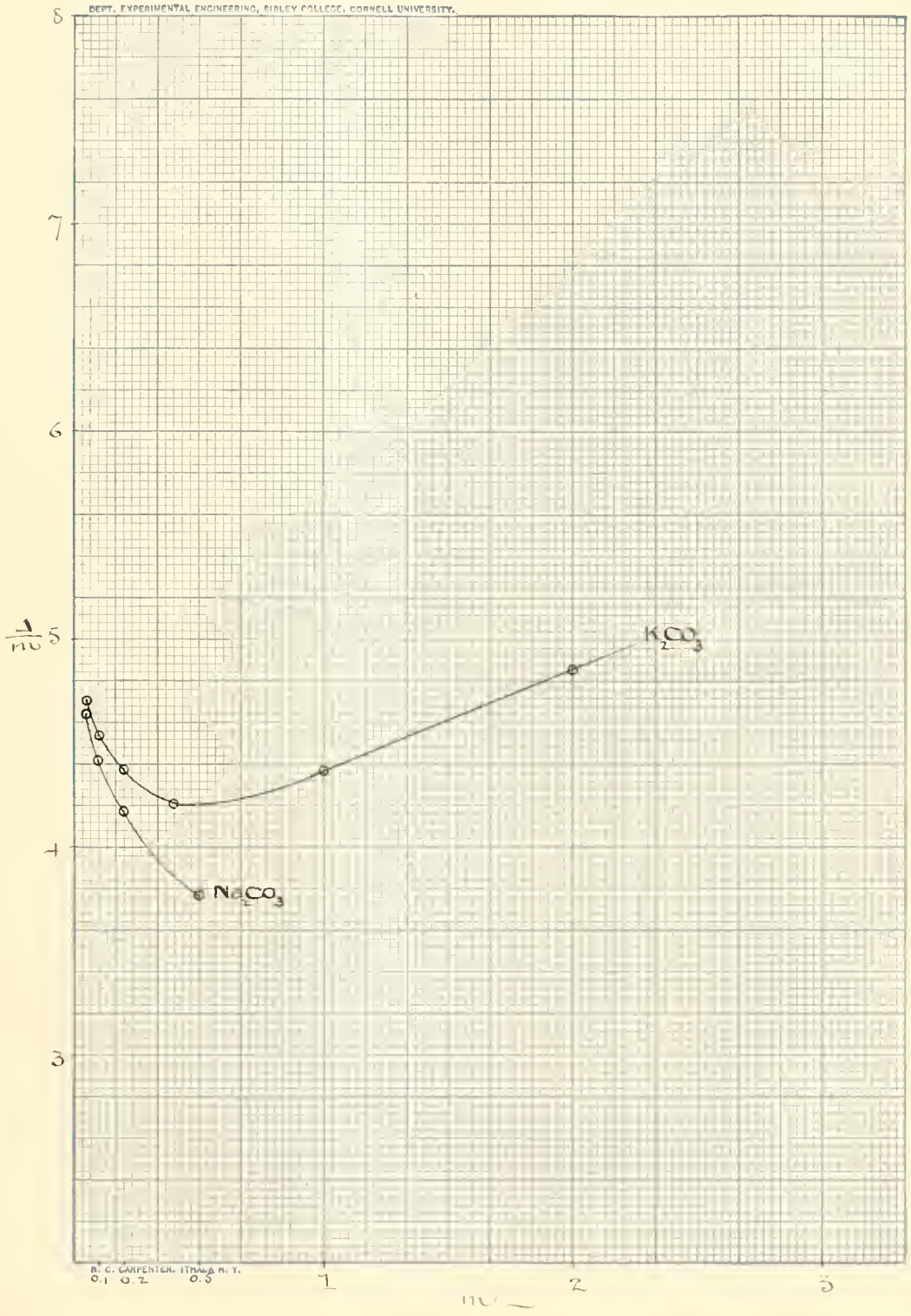
v	μ_0
20	114.04
10	104.34
5	95.54
2.5	87.05
1	74.25
0.5	61.57

REFRACTIVITY MEASUREMENTS.

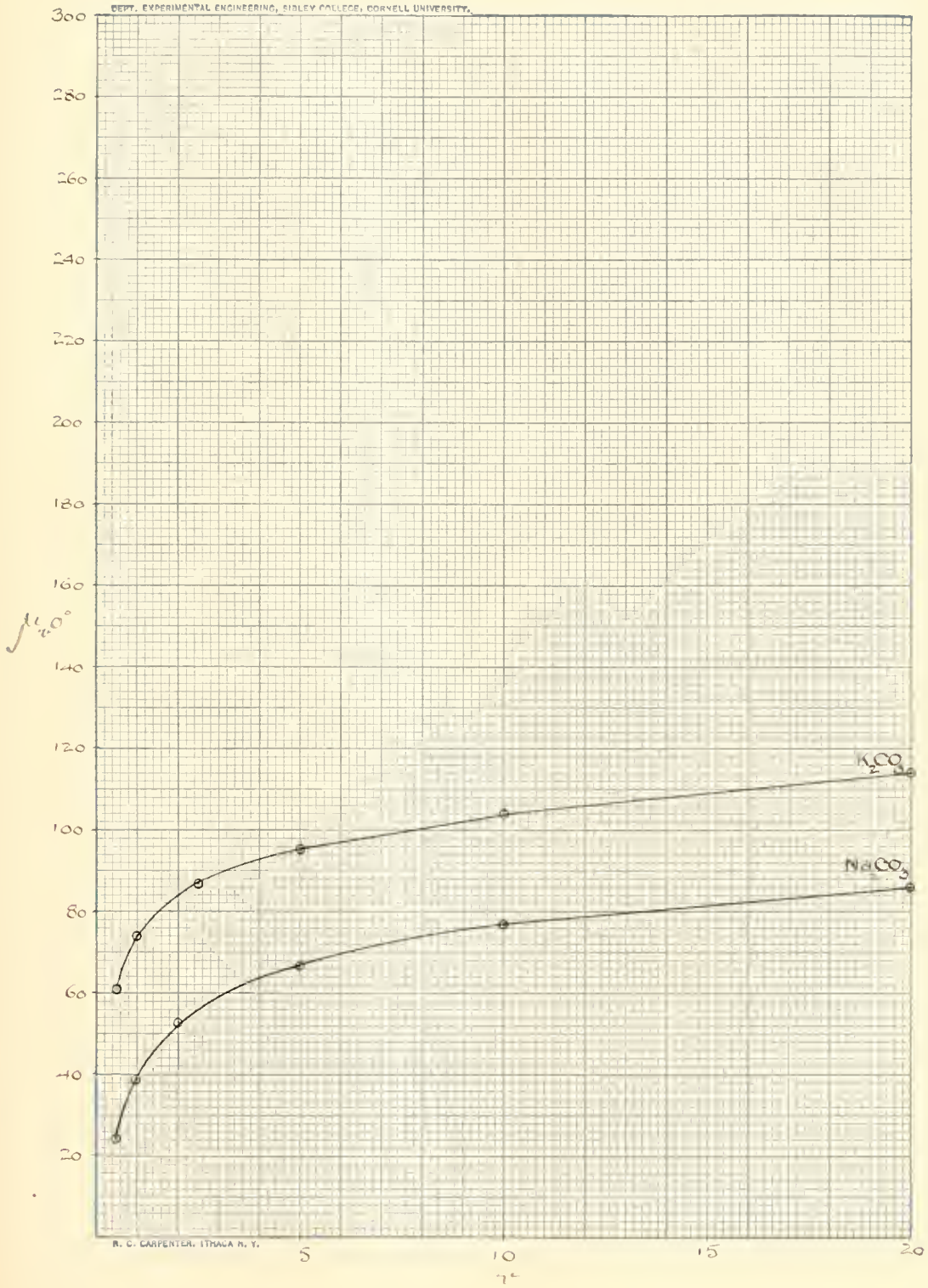
m	x	n
0.05	67° 10'	1.32632
0.10	66 54	1.32758
0.20	66 26	1.32980
0.40	65 35	1.33395
1.00	63 18	1.34553
2.00	60 12	1.36219

BOILING-POINT MEASUREMENTS.

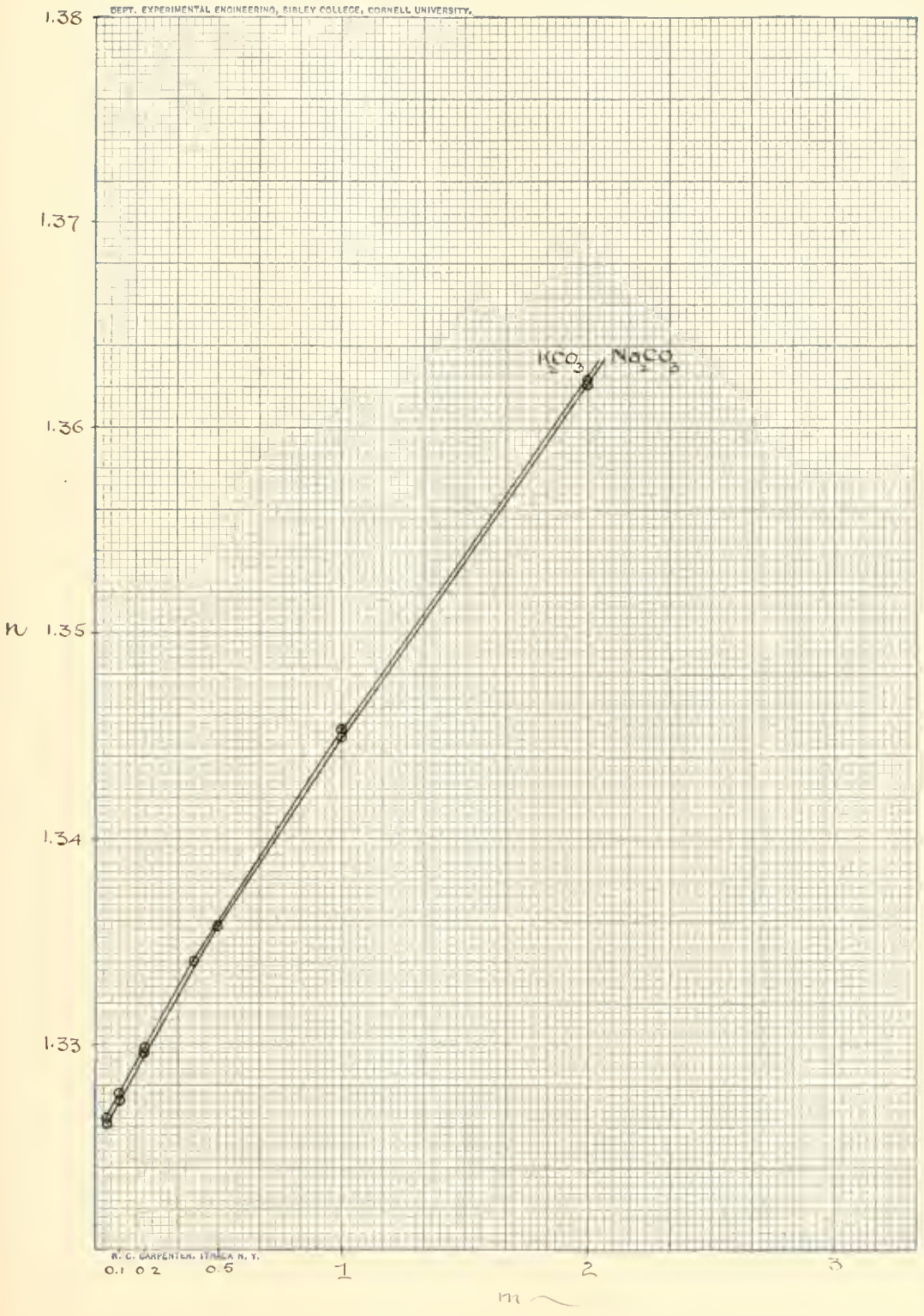
m	Δ	Barom. Press.	$\frac{\Delta}{m}$
0.05	0.055	765.5 mm	1.100
0.10	0.102	765.5	1.020
0.20	0.194	765.2	0.970
0.40	0.378	765.0	0.945
1.00	1.080	764.5	1.080
2.00	2.680	764.5	1.340



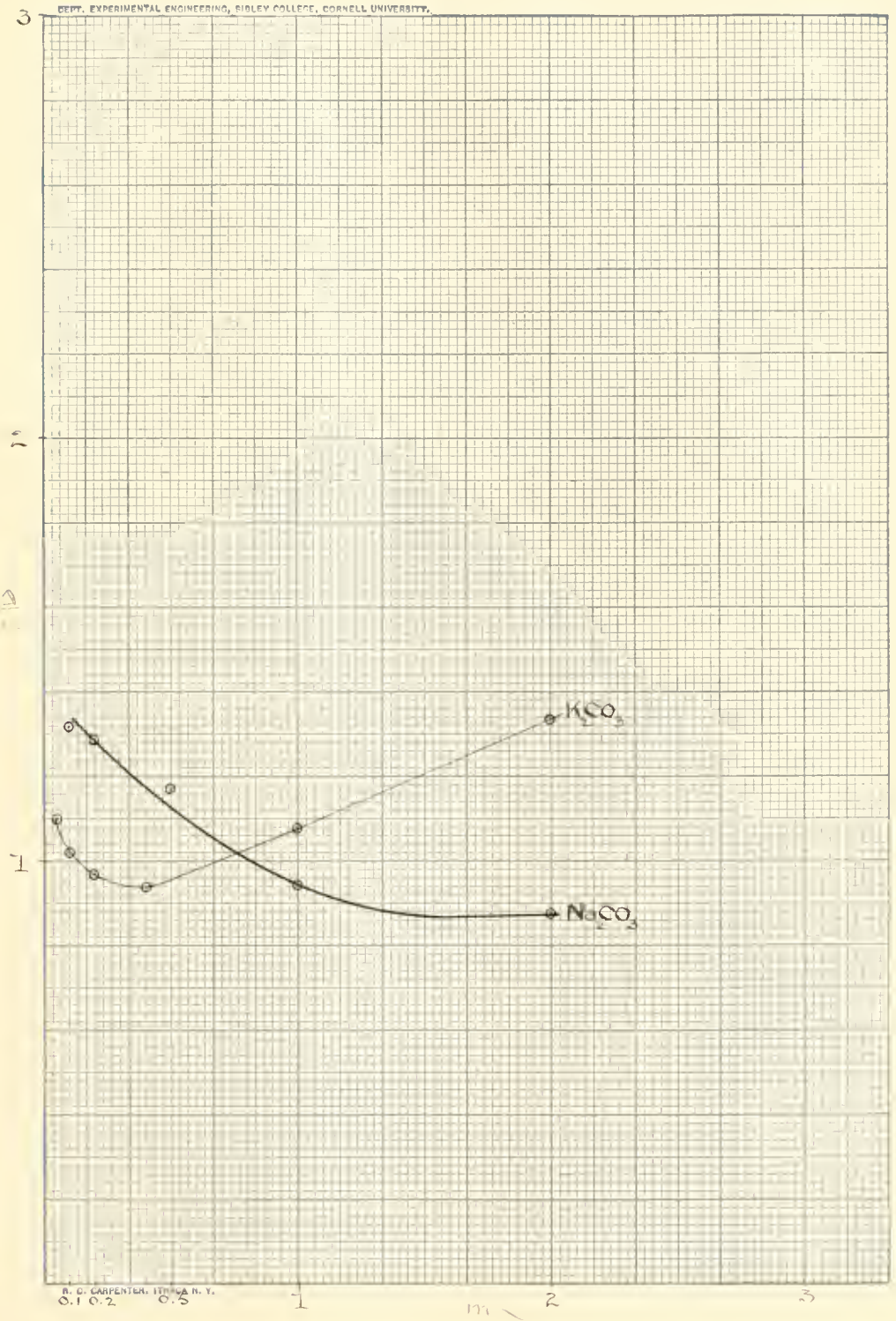
Freezing Point Curves for the Carbonates.



Conductivity Curves for the Carbonates.



Refractivity Curves for the Carbonates



Boiling-Point Curves for the Carbonates.

PHOSPHORIC ACID.

H_3PO_4. 98.03

The acid was obtained from Bender and Hobein in a well crystallized condition. It was dissolved in pure water and the strength of the solution determined by means of gravimetric analysis, the phosphoric acid being weighed as magnesium pyro phosphate.

The analysis was checked by means of a pyknometric determination of its specific gravity.

Here as in all similar cases care was taken to dilute an appreciable volume of the mother solution and to employ a large volume of the diluted solution for the analysis.

From the standardized mother solution the lesser concentrations were obtained by dilution.

FREEZING-POINT MEASUREMENTS.

m	$\frac{\Delta}{m}$	
	1) Loomis	2) Jones
0.05	2.490	———
0.06	——	2.65
0.10	2.358	2.35
0.15	———	2.32
0.20	2.249	——

m	s	k	Δ	$\frac{\Delta}{m}$
0.52	1.138	0.027	1.111	2.137
1.04	2.475	0.007	2.468	2.373
2.08	5.408	0.010	5.398	2.595
3.12	9.463	0.008	9.455	3.030

1) Phys. Rev. 3. 279
2) Zeit. Phys. Chem. 12. 623.

CONDUCTIVITY MEASUREMENTS.

v	Λ_v
15.39	82.18
7.68	62.06
3.85	50.38
1.92	42.92
0.96	37.70
0.48	34.89
0.32	33.16

REFRACTIVITY MEASUREMENTS.

m	x	n
0.065	67° 18'	1.32570
0.130	67 12	1.32616
0.260	66 55	1.32750
0.520	66 30	1.32949
1.040	65 39	1.33362
2.080	64 00	1.34191
3.120	62 30	1.34974

POTASSIUM DI-HYDROGEN PHOSPHATE.

KH_2PO_4 136.17

The specimen used came from Kimer and Amend and was found to be chemically pure. It was dried in an air-bath for three days at 100° C and was then preserved in vacuo over sulphuric acid. The mother solution was made up by direct weighing and the lesser concentrations obtained by dilution.

Owing to the slight solubility of the salt it was found to be impossible to extend the freezing-point measurements beyond normal concentration.

FREEZING-POINT MEASUREMENTS

m	$\frac{\Delta}{m}$
	1) Loomis
0.01	3.58
0.02	3.60
0.05	3.48
0.10	3.37
0.20	3.22

m	s	k	Δ	$\frac{\Delta}{m}$
0.5	1.525	———	1.525	3.050
1.0	2.800	0.020	2.780	2.780

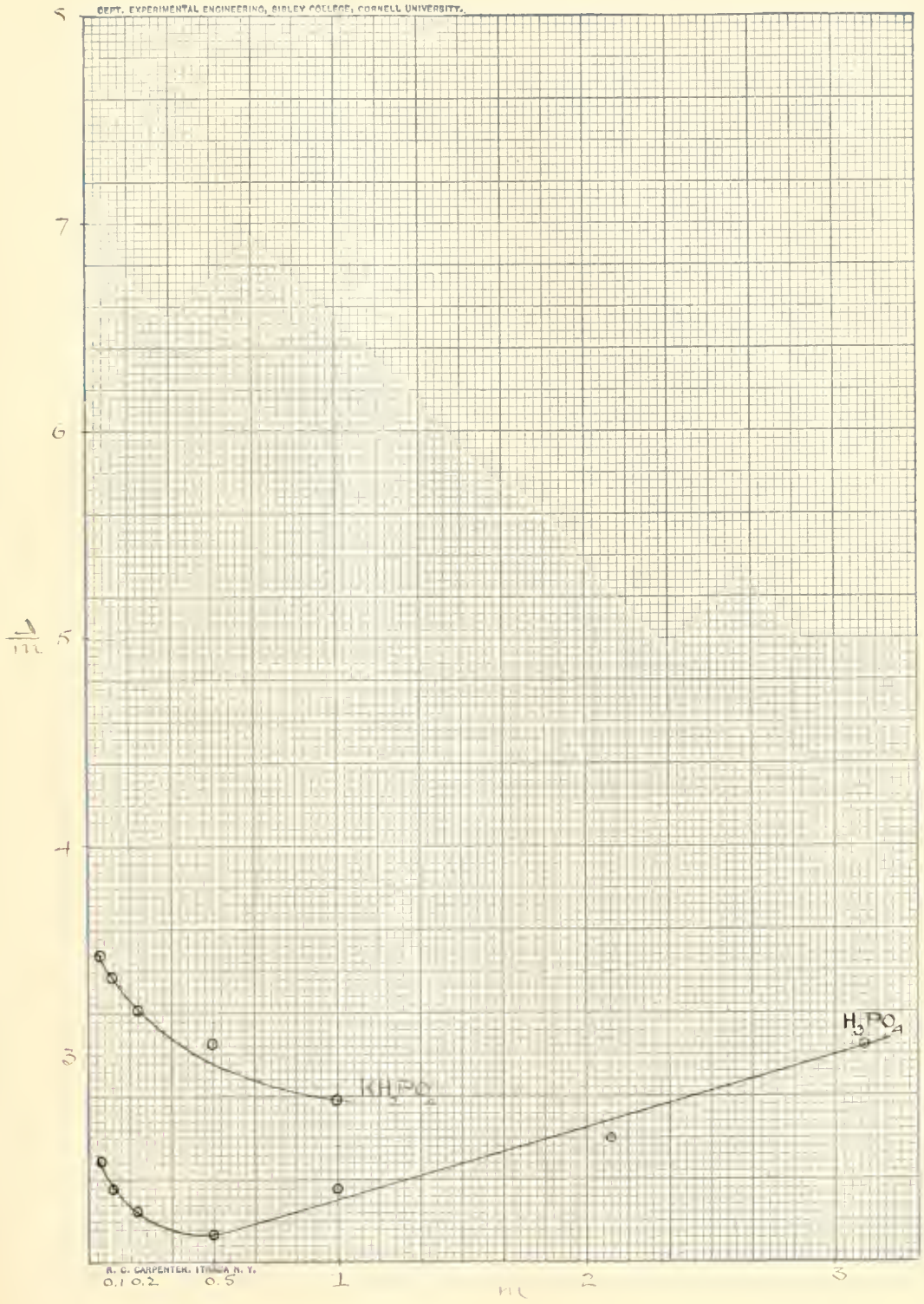
CONDUCTIVITY MEASUREMENTS.

v	μ_v
20.0	51.00
10.0	46.71
5.0	42.45
2.0	38.24
1.0	32.21
0.667	26.98

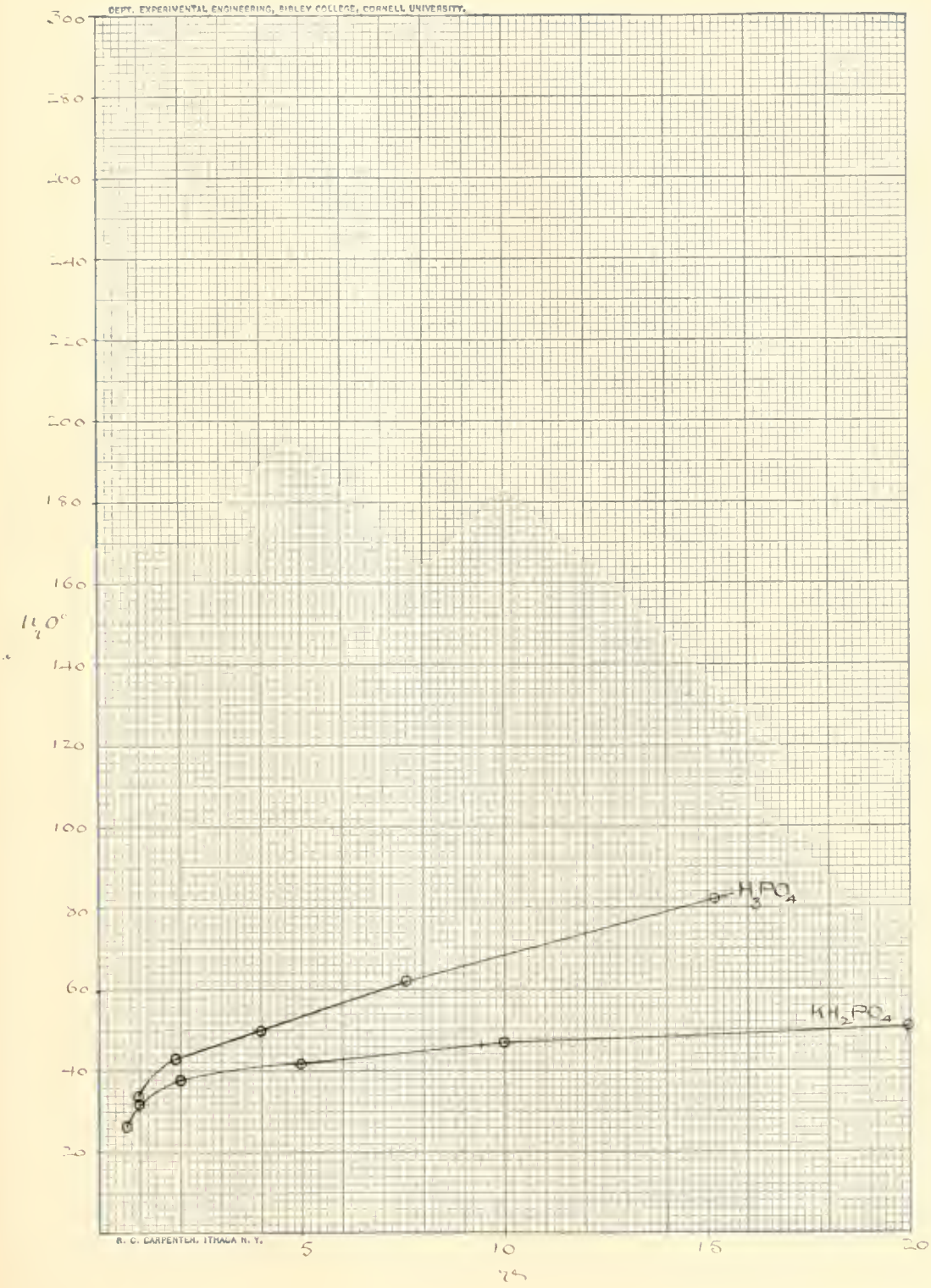
1) Phys. Rev. 4.284

REFRACTIVITY MEASUREMENTS.

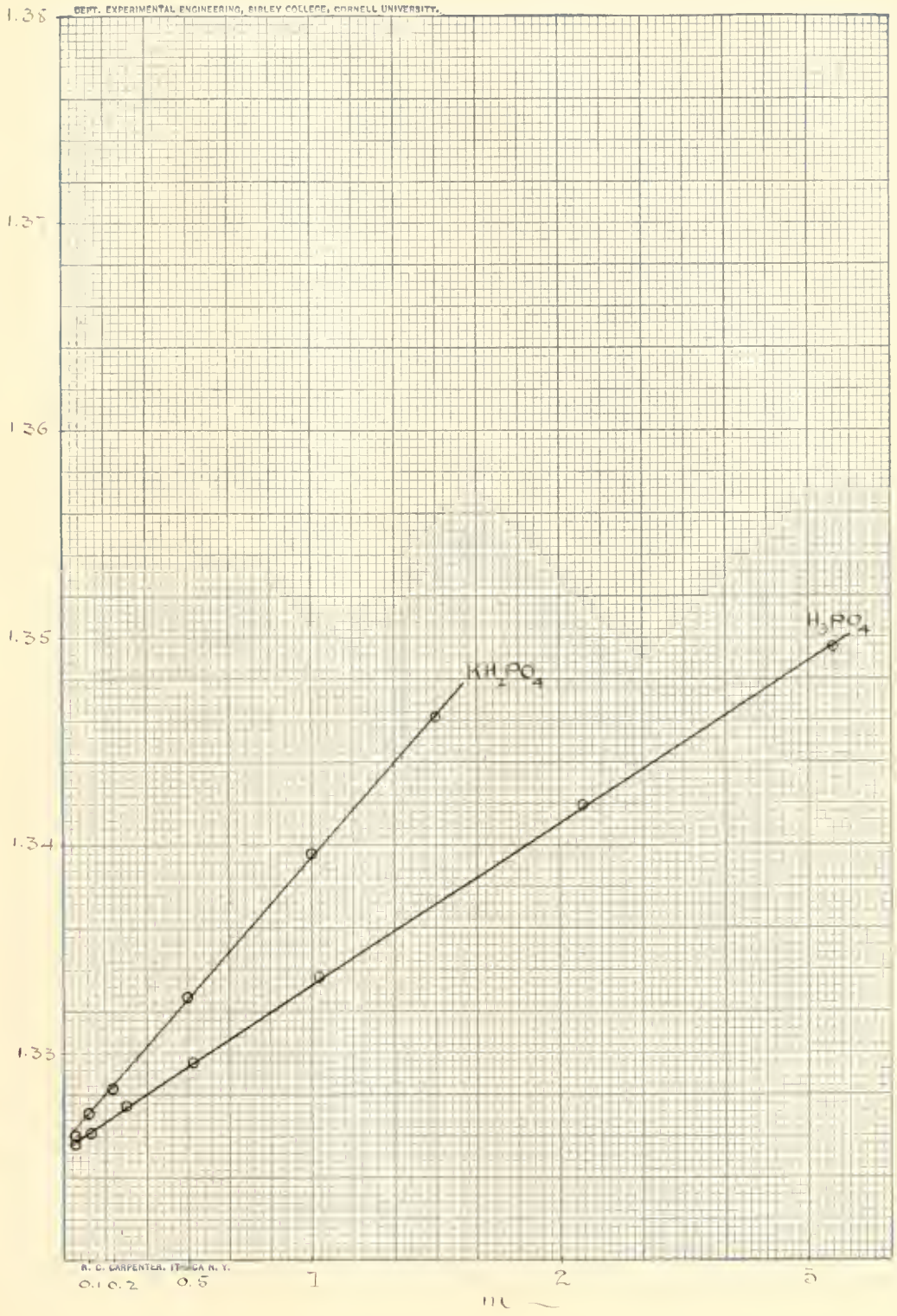
m	x	n
0.05	67° 15'	1.32593
0.10	67 00	1.32711
0.20	66 45	1.32829
0.50	65 50	1.33272
1.00	64.25	1.33978
1.50	63 10	1.34623



Freezing-Point Curves for the Phosphates.



Conductivity Curves for the Phosphates—



Refractivity Curves for the Phosphates.

SODIUM HYDROXIDE.

NaOH- 40.06

The mother solution of sodium hydroxide was made from a chemically pure specimen obtained from Bender and Hobein. The exact strength pf the solution was determined by titration with N/5 sulphuric acid, great care being taken to work with volumes sufficiently large to minimize errors in dilution and burette readings. The more dilute solutions were prepared by dilution from the mother solutions. The solutions were used as soon as possible after preparation to avoid error, owing to the solvent action of the alkali on the glass of the containing bottles and to the absorption of carbon dioxide from the air.

FREEZING-POINT MEASUREMENTS

m	$\frac{\Delta}{m}$	
	1) Loomis	2) Jones
0.02	3.46	——
0.05	3.45	3.56
0.10	3.41	3.42
0.20	3.41	——

m	s	k	Δ	$\frac{\Delta}{m}$
0.52	2.175	0.026	2.149	3.466
1.24	4.492	0.043	4.449	3.588
1.86	7.175	0.036	7.139	3.838
2.48	9.775	0.010	9.765	3.937

1) Phys. Rev. 4.282
2) Zeit. Phys. Chem. 12. 623

CONDUCTIVITY MEASUREMENTS.

v	Λ_0
16.0	117.00
8.0	115.00
2.0	104.00
0.81	93.46
0.54	80.08
0.40	71.43

REFRACTIVITY MEASUREMENTS.

m	x	n
0.124	67° 2'	1.32695
0.248	66 45	1.32829
0.620	65 55	1.33231
1.240	64 38	1.33869
1.860	63 30	1.34449
2.480	62 25	1.35018

POTASSIUM HYDROXIDE

KOH. 56.0

Chemically pure potassium hydroxide from alcohol was used in the preparation of the mother solution. The concentration of this original solution was determined by titration with N/5 sulphuric acid and the dilutions made in the usual manner. The same precautions were taken as with sodium hydroxide to prevent the solutions becoming contaminated with silicates and carbonates.

FREEZING-POINT MEASUREMENTS.

m	$\frac{\Delta}{m}$	
	1) Loomis	2) Jones
0.05	3.44	3.58
0.10	3.43	3.47
0.20	3.43	—

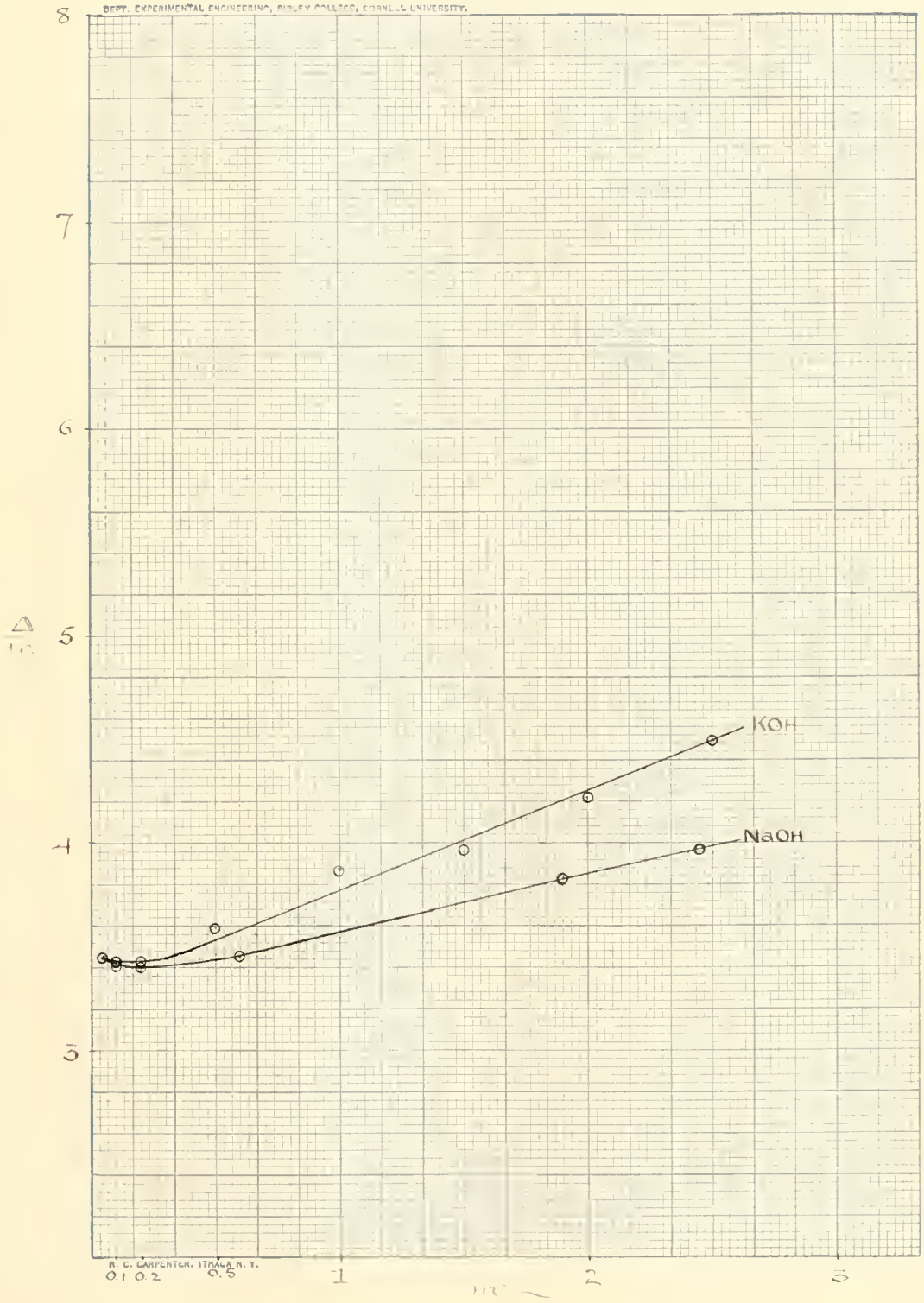
1) Phys. Rev. 4. 282

2) Zeit. Phys. Chem. 12. 623

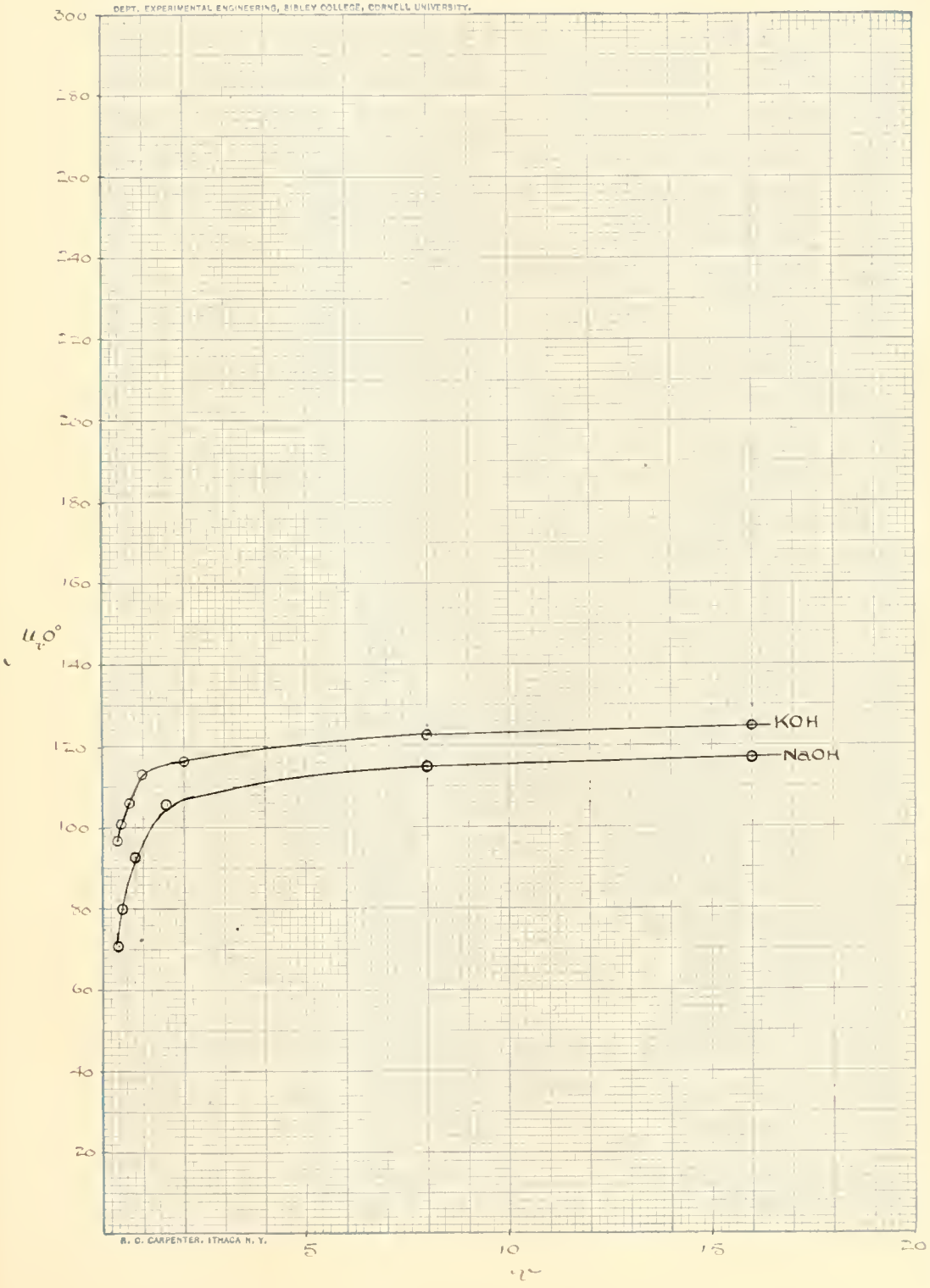
m	s	k	Δ	$\frac{\Delta}{m\sigma}$
0.5	1.810	0.002	1.808	3.616
1.0	3.920	0.039	3.881	3.881
1.5	5.975	0.011	5.964	3.976
2.0	8.492	0.006	8.486	4.243
2.5	11.308	0.006	11.302	4.521

CONDUCTIVITY MEASUREMENTS.

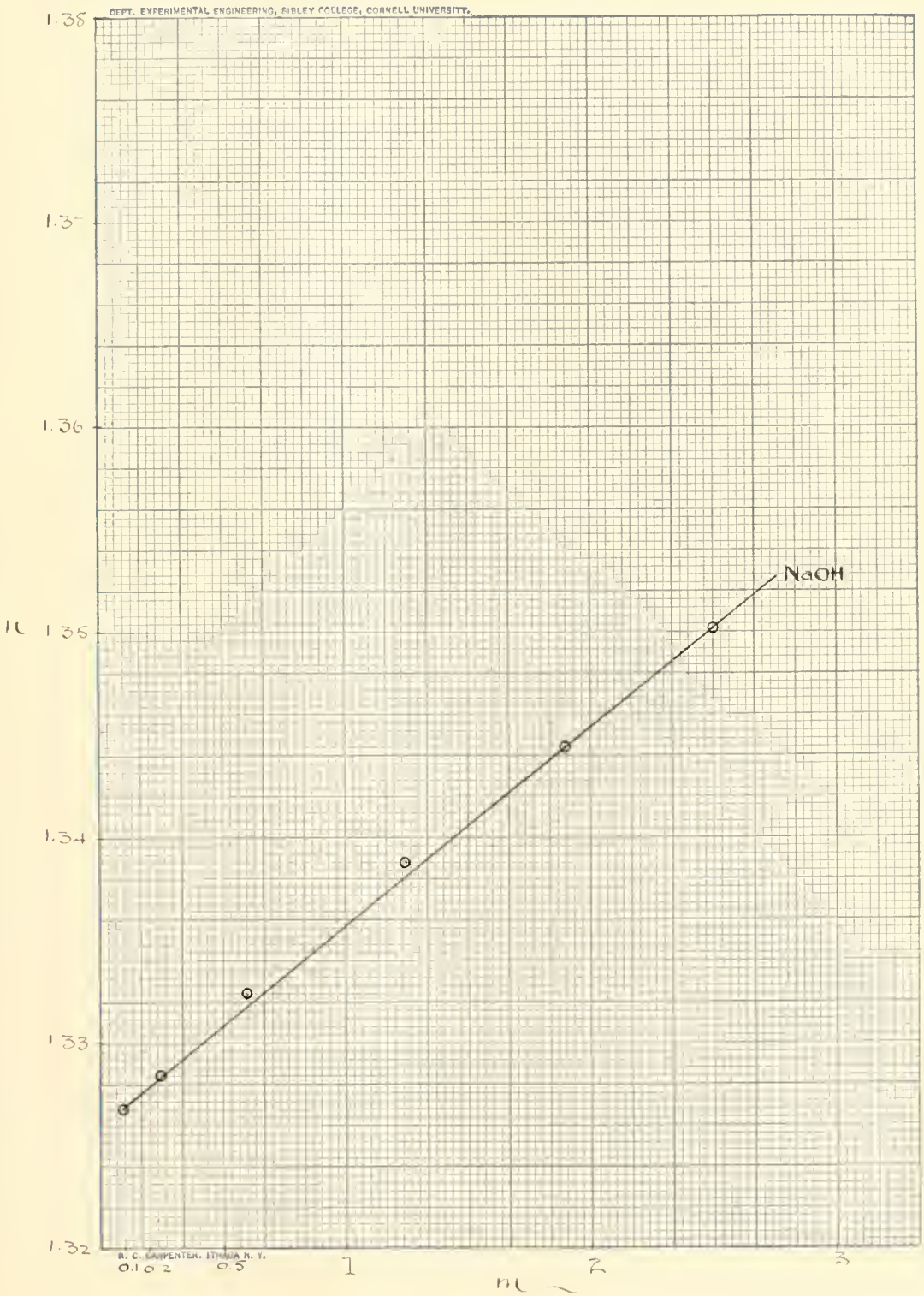
v	$\mu_{18}{}^{\circ}$
16.0	125.30
8.0	122.80
2.0	118.40
1.0	113.33
0.667	106.35
0.500	101.15
0.400	97.40



Freezing-Point Curves for the Hydroxides.



Conductivity Curves for the Hydroxides.



Refractivity Curves for the Hydroxides~

S U M M A R Y.

From the work previous to this investigation and from the data herewith presented, it is seen that with but few exceptions every electrolyte gives abnormal molecular depressions of the freezing-point. Among these exceptions are sodium, potassium and ammonium nitrates, and potassium di-hydrogen phosphate.

Among the chlorides we observe that those of the second group in the periodic system of classification give greater molecular depressions than those of the first group. We also observe that the curve for hydrochloric acid lies considerably above the corresponding curves for lithium, ammonium, sodium and potassium chlorides. The relation between lithium and the members of the second group is clearly shown by the curves for lithium chloride and lithium nitrate which resemble the curves for the corresponding salts in the second group more closely than the analogues of the first group. The relation is very marked in the case of lithium nitrate.

Owing to limited solubility the study of the sulphates was not possible to any extent so that it cannot be stated whether these salts exhibit the phenomenon.

In general we may say that the freezing-point curve for any acid lies above those of the salts which it forms with the metals of the first group, while it lies below the curves for its second group salts. Further it will be seen that the molecular depressions for similar substances are arranged in the order of their molecular weights. The conductivity curves for all of the substances studied are perfectly normal throughout, showing absolutely no peculiarities in the region of dilution where the minimum of molecular depression manifests itself. The refractivity curves are nearly straight lines. In the few boiling-point curves which are given there is a more or less marked minimum but as has been pointed out hitherto no great reliance can be placed upon the results obtained by the boiling-point method.

CONCLUSIONS.

Apparently Arrhenius was the first to offer any explanation of the increase in molecular lowering from a certain point with increase in concentration. As has been indicated in the historical introduction to this investigation Arrhenius observed the abnormality in solutions of cane sugar, dextrose, mannite, and glycerine, all of which are non-electrolytes. It was to this class of substances that he applied his theory. To quote his own words:- "Wir finden also, dass nach der Anschauung, dass die Anziehung zwischen Wasser und gelöstem Körper den osmotischen Druck verursacht, dieser dem Quadrat der Konzentration proportional sein muss. Nach der herrschenden Kinetischen theorie des osmotischen Druckes muss er aber der Konzentration direckt proportional sein. Wirken beide Umstände gleichzeitig, so wird

$$\Pi = AK + BK^2$$

(Wo Π osmotischen Druck, K Konzentration, A die Gaskonstante mal der Temperatur und B eine Konstante ist, welche ein Mass giebt für die Differenz zwischen den Anziehungen: Lösungsmittel- gelöster Körper und gelöster Körper- gelöster Körper)

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1) Zeit. Phys. Chem. 10.64

"Wenn K sehr klein ist, verschwindet BK^2 gegen AK, d.h. in diesem Fall gelten dieselben Gesetze als für ideale Gase. Je nachdem B positiv oder negativ ist, muss der Quotient $\frac{\pi}{K}$ (für nicht dissociierte Körper) mit wachsenden K zu- oder abnehmen. Beide Fälle kommen recht häufig vor, [Wenn Wasser als Lösungsmittel verwendet wird] so ist für gewöhnlich B positiv, und es ist schon lange hervorgehoben, dass dies auf starker Anziehung zwischen Wasser und gelöstem Körper beruhen kann. Auch ist auf einige Umstände hingewiesen worden, welche eine solche Ansicht wahrscheinlich machen. Zu diesen kommt jetzt ein anderer Umstand, nämlich dass der Quotient $\frac{\pi}{K}$ wirklich nach den Versuchen sehr nahe durch einen linearen Ausdruck A + BK dargestellt wird, wie ich schon hervorgehoben habe."

In the same communication he showed that proportionality exists between osmotic pressure and freezing-point lowering. Since freezing-point lowering and osmotic pressure are proportional $\frac{\Delta}{K}$ (Δ= lowering) would increase which is in entire agreement with experimental facts.

The next explanation which was offered applied equally to electrolytes and non-electrolytes.

Jones and Chambers[1] after studying the behavior of the chlorides and bromides of the alkaline earths concluded that the phenomenon was to be explained by assuming the combination of the dissolved substance with water to form hydrates. They put the question to themselves "How is it then possible to account for these abnormally great depressions of the freezing-point?" This they answer as follows:- In concentrated solutions these chlorides and bromides must take up part of the water forming complex compounds with it and thus removing it from the field of action as far as freezing-point lowering is concerned.

The total amount of water present, which is now acting as a solvent is diminished by the amount taken up by the chloride or bromide molecules.

The lowering of the freezing-point is thus abnormally great because a part of the water is no longer present as solvent but is in combination with the chloride or bromide molecules.

By assuming that a molecule of the halide is in combination with a large number of molecules of water, it is possible to explain all of the freezing-point results obtained."

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1) Am. Chem. Jour. 23-103.

Owing to the similarity of many of the freezing-point curves to the curves obtained by Amagat[1] for gases the author attempted to apply the well known equation of Van der Waals

$$(p + \frac{a}{v^2})(v - b) = RT$$

but it soon became evident that this without some radical modifications cannot be employed. After careful consideration of the problem the hydrate theory of Jones is advanced as a tentative explanation of the phenomenon. It must be said in defense of this theory that the conductivity and refractivity measurements tend to confirm it as does also the work of Jones[2] on the hydrates of sulphuric acid.

It is the intention of the author to extend these observations, using solvents other than water and it is through such studies that he hopes to gain some insight into the dynamics of solution.

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1) Ann. Chim? Phys. 19,379.
2) Zeit. Phys. Chem. 13.419.

-: BIOGRAPHY :-

FREDERICK HUTTON GETMAN, the author of this dissertation was born in Oswego, New York on February 9, 1877. At the age of twelve he moved with his parents to Stamford, Connecticut where he attended school and prepared for college. In 1893 he entered the Rensselan Polytechnic Institute at Troy N. Y. where he remained for three years. In 1896 he matriculated in the School of Chemistry at the University of Virginia graduating in 1897 in analytical and industrial chemistry.

In the winter of 1898 he was appointed instructor in mathematics in the High School at Stamford, Conn. and in the following year was appointed instructor in chemistry and physics in the same institution. In the autumn of 1901 he entered the Johns Hopkins University as a graduate student in chemistry, his subordinate subjects being physical chemistry and mathematics. In June 1902 he was appointed Fellow In Chemistry in this University.

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